RAPID METHODS
FOR THE
Chemical Analysis of Special Steels, Steel-Making Alloys, Their Ores and Graphites

BY

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INTRODUCTION TO THE THIRD EDITION

THE author wishes again to emphasize the generalization, or rule, which he believes should guide those who wish to experiment in the alloying of iron with other elements. The general statement can be expressed as follows: "If iron be combined by fusion with notable quantities of an element whose melting-point is very much below that of iron, the tendency is to produce a metal of inferior physical properties, but if iron be combined with an element whose melting-point is nearly that or higher than that of iron, then the tendency is to produce a metal of superior physical properties." (See Introduction to second edition.)

The following are some new features of the third edition:

(1) A new qualitative test for cobalt in steel. Page 2.

(2) The latest details of the author's routine method for vanadium in vanadium and chrome-vanadium steels. Page 21.

(3) Rapid bath test for chromium. Pages 26 and 28.

(4) Modified bath test by persulphate for vanadium. Page 28.

(5) Walter's method combined with the author's method, using potassium ferricyanide as an internal indicator.

(6) The author's new method for small (or large) amounts of chromium and vanadium, removing the bulk of the iron with ammonia. The vanadium can be also separated in this method from a large amount of chromium as the vanadium is precipitated along with the *firs* portion of the chromium. This makes possible the accurate determination of a small amount of V in the presence of a large amount of Cr, as the most of the latter can be left behind in the filtrate together with the Fe. See pages 30 and 31. The neutralization is stopped as soon as the first part of the Cr hydroxide appears. For example, suppose it is desired to determine about 0.10 V in the presence of 15.00 per cent Cr.

(7) The complete analysis of ferro-vanadium, rewritten for Al, Fe, Mn, P, Si, and V. Pages 34 to 39.

(8) An entirely new modification to get the total phosphorus in ferro-vanadium and vanadium steel, using a faintly ammoniacal water solution of ammonium molybdate.

(9) A new method for separation of the bulk of the titanium from the iron by ammonia. Pages 30 to 31.

(10) The author's method for the determination of sulphur by heating the substance such as finely divided steel, drillings or millings, ores, minerals (and sulphates by ignition of the powder) in a stream of hydrogen saturated with HCl has been extended to a wide range of materials: At a temperature of about 950° C. following reaction takes place:

$$BaSO_4+2HCl+8H=BaCl_2+4H_2O+H_2S.$$

See pages 122 to 129.

(11) The methods as used by the author for Mg, Ca, Pb, As, Bi, Cu, Sb, Ta, Mo, and S in tungsten ores have been added. See pages 97 to 113.

(12) Persulphate method for manganese for all percentages of manganese up to 80 per cent, or higher. Page 250 and page 136.

(13) New cuts of the author's design of rheostat and muffle furnace and carbon combustion furnace. Page 119.

(14) The determination of large and small amounts of tantalum and tungsten in the presence of each other. Page 138.

(15) The complete analysis of Wulfenite ore. Page 168.

(16) Arsenic in steel. Page 162.

(17) The determination of Al, Fe, V, and Cr in ferro-chrome is rewritten. Pages 174 to 186.

(18) The author's method for the determination of large and small amounts of Al and Zr in steel by first removing the bulk of the iron with ammonia. Pages 189 to 191.

(19) The complete analysis of zirconium-nickel-aluminun-iron alloy. Pages 194 to 201.

(20) The analysis of crude zirconia. Pages 202 to 204.

(21) The determination of oxygen and arsenic in copper. Pages 218 and 219.

(22) The determination of boron in iron following Wherry as modified by J. M. Lindgren. Pages 253 and 255.

(23) Rapid volumetric method for manganese in steel in the presence or absence of much chromium. Accurate to at least 15 per cent of manganese. Pages 343 to 347.

(24) The use of zirconia composition crucibles as a substitute for platinum crucibles in the determination of silicon in plain steel, and pig iron. Page 350.

(25) A new method for uranium in steel by removing the bulk of the iron with ammonia. Pages 363 to 365.

(26) New cuts of the author's combustion train and apparatus for weighing CO_2. Pages 276, 278, 279.

(27) The author's present routine method for nickel. Page 232.

(28) The complete analysis of pitchblende. Page 270.

(29) The determination of alkalies in clay. Pages 411 to 413.

(30) The complete analysis of clays. Page 407.

(31) The determination of cerium in ferro-cerium and cerium steel. Pages 533 to 538.

In all there are considerably more than one hundred additional pages of new material not found in either of the previous editions; and a net increase of the size of the book to the extent of also more than 100 pages.

(32) A chapter has been added on the microscopic examination of steel. Pages 492 to 503.

PITTSBURGH, PA.,
July 7, 1920.

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RAPID METHODS FOR THE CHEMICAL ANALYSIS OF SPECIAL STEELS, STEEL-MAKING ALLOYS, THEIR ORES, AND GRAPHITES

CHAPTER I

QUALITATIVE TESTS FOR CHROMIUM, TUNGSTEN, NICKEL, MOLYBDENUM, ETC.

Dissolve 0.200 gram of the sample with 5 c.c. 1 : 3 sulphuric acid in 152.4 (6 inches) by 16 mm. test tube. Also 0.200 gram of a plain carbon steel in the same way. Place the two tests in boiling water for a half hour.

The plain carbon steel will be free from black sediment and practically water white as to color. If the unknown contains as little as 0.2 or 0.3 per cent of chromium it will look distinctly greener than the known steel. Nickel also produces this effect, but the color is not so marked.

If the steel has 0.100 to 0.3 per cent of tungsten a black insoluble residue will be found in the bottom of the tube. This black sediment forms also with similar amounts of molybdenum and phosphorus. But on addition of 1 c.c. of 1.20 nitric acid to such a solution the black entirely disappears if due to the presence of the two last named elements. The black precipitate, if caused by a small quantity of tungsten, on addition of the nitric acid, changes to a yellow one. If the amount of the latter is small it is better to put the test tube back on the water bath and permit the tungstic acid to settle for two hours, when it can be seen plainly as a yellow spiral thread rising up through the solution by giving the test tube a rotary motion. The black residue of phosphide can be recognized by filtering it out and dropping 1 : 1 hydrochloric acid on it, when the characteristic odor of phosphine is obtained. Or it can be dissolved off the filter with 1.20 nitric acid and the filtrate precipitated with molybdate solution after boiling it with a slight excess of potassium permanganate. Finish as in plain steel to get the yellow precipitate. If steels are quite high in silicon, the silicic acid and the carbon, together, produce black flakes that float about. They turn to white ones on being heated with 1.20 nitric acid on a water bath for an hour or two.

The annealed test for chromium is given under " Annealing of Steel." (See page 419.)

Molybdenum.*—A further qualitative test for the latter element is as follows: Dissolve 0.500 gram of sample in 25 c.c. of 1 : 1 hydrochloric acid. Boil till the action ceases, using a 254 by 25.4 mm. (10 by 1 inch) tube. Heat further with 2.5 grams of potassium chlorate until a clear solution has been obtained or the residue, if any, is a bright yellow. Add an equal volume of water. Filter without washing. Dissolve 10 grams of potassium hydroxide in 10 c.c. of water. Add this to the filtered solution. Boil for five minutes. Filter. Do not wash. Pour 8 c.c. of this filtrate into a 254 by 25.4 mm. tube. Add conc. hydrochloric acid until crystals form. Dilute with water to 30 c.c. Add a few grains of granulated tin. Heat to the *first* indication of boiling; remove from heat immediately and cool. Add to the cold solution 2 c.c. of potassium sulphocyanate. A light brownish red indicates 0.2 or 0.3 per cent of molybdenum. A distinct red indicates 1 to 2 per cent and a deep red higher amounts of molybdenum. This is a fine test, but if the mistake is made of boiling the solution too long with the tin scarcely any color is obtained. Bring, therefore, to incipient boiling, only, after putting in the grains of tin. Then remove at once from the fire and test with the KCNS as already described. For *nickel* the quantitative analysis as given on page 232 is so rapidly carried out that it constitutes an easy qualitative test also.

For qualitative tests for titanium and vanadium see page 4. For qualitative tests for copper in steel see page 207. For qualitative tests for copper in ferro-vanadium see page 9. For qualitative test for nickel in steel see, also, page 7.

Qualitative Test for Cobalt.—Dissolve 0.200 gram of the steel in 5 c.c. of 1 : 1 HCl in a 154.2 (6 in.) × 16 mm. tube on a water bath. At the same time in the same manner dissolve 0.200 gram of plain carbon steel. If the unknown steel contains even as much as 0.05

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* See also page 160 for further details of the qualitative test for molybdenum in steel.

per cent of cobalt it will show a distinct green *when hot* whereas the plain steel will be a golden yellow color. This yellow color can be eliminated by adding a few grains of metallic tin to the tests. It is characteristic of the cobalt that this green color will fade away when the solution cools down, and return again if reheated. If 1 gram of sample is dissolved in 10 c.c. of the hydrochloric acid and, after all action is over, a few grains of metallic tin are used to keep back the color of ferric iron, as little as 0.05 per cent Co can easily be detected. Nickel gives so much less color that, in a 0.200 gram test, as much as 5 per cent of nickel gives practically no interference with the cobalt test if a little tin is added to keep the iron all reduced. Cobalt does not give this delicate test in sulphuric acid solution. Chromium interferes greatly. It should be removed by peroxidation before making the test. See also page 372.

Qualitative Test for Nickel.—Dissolve 0.5 gram of the steel as given for vanadium on page 5. When the red fumes are gone, cool; add 2 grams of citric acid and then ammonia until the solution is ammoniacal and clear. Now introduce a solution of dimethylglyoxime of the strength given on page 231. A scarlet precipitate will form if nickel is present. See also page 372 if the chemist wishes to first remove the iron before adding the "dimethyl," which is a better way if the per cent of nickel is very small.

Qualitative Test for Titanium in the Presence of Vanadium.—Dissolve the steel as for vanadium as given on page 5 but in a small boiling flask, using 0.5 gram of sample. Then peroxidize as described on page 35, taking proportionately smaller amounts of the sodium peroxide and carbonate. Redissolve the iron hydroxide, after washing it with peroxide water, and peroxidize again, and so on until some of the filtrate from the iron hydroxide no longer gives a vanadium test with H_2O_2 on being boiled down to one-half with twice its bulk of conc. nitric acid. The iron hydroxide can then be dissolved with 1.20 nitric acid and be tested with hydrogen peroxide for Ti. The iron hydroxide will contain all of the Ti, free from V.

CHAPTER II

*ANALYSIS OF CHROMIUM AND VANADIUM STEEL AND FERRO-VANADIUM

THE determination of vanadium in the presence of tungsten, titanium, chromium, nickel, manganese, silicon, molybdenum, copper and aluminum has been studied by the author. It has been the latter's aim to produce modified methods that combine speed, simplicity and accuracy. The underlying reactions are well known and have been variously applied by different chemists.

QUALITATIVE TESTS

Absence of Titanium.—A qualitative test for vanadium can be completed in a half hour or less, even in the presence of 4 per cent of chromium, although there be but 0.05 per cent of vanadium in solution. Dissolve 0.500 gram of steel in a 254 by 25.4 mm. test tube (10 by 1 inch) in 10 c.c. 1 : 3 sulphuric acid, heating until action ceases, adding a little water, if necessary, to dissolve any sulphate of iron that may separate during the boiling. Five c.c. of concentrated nitric acid are used to oxidize the iron and hypovanadic acid. Heating is continued until red fumes disappear. If tungsten be present, filter through paper. Filter without washing. Pour some of the filtered or unfiltered fluid, as the case may be, into two 152 by 16 mm. test tubes, allowing about 5 c.c. of the solution to each tube. To one of these portions add 5 c.c. of sodium peroxide dissolved in dilute sulphuric acid. To the other add 5 c.c. of water. The portion to which the sodium peroxide was added assumes a reddish brown shade if vanadium is present.

If there be enough chromium to give the solution a dark green tint, then hold the tubes against an illuminated white shade. The vanadic solution containing peroxide will plainly show a browner tint than its mate, to which no peroxide was added. The white shade greatly lessens the interference of the chrome green. The peroxide is prepared by dissolving 3.5 grams of sodium peroxide in 125 c.c. of 1:3 sulphuric acid and diluting with distilled water to 500 c.c. Add the water last, when preparing the peroxide solution.

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* From a paper read before the Pittsburgh section of the American Chemical Soc., Jan. 23, 1908.

THE DETERMINATION OF CHROMIUM AND VANADIUM IN STEEL

The *quantitative* determination of vanadium and chromium in most varieties of steel can be made in a comparatively simple way. The writer proceeds as follows: Two grams of steel are heated in a mixture of 30 c.c. of 1 : 3 sulphuric acid and 20 c.c. of water in a 600 c.c. beaker. When the first action is over, 30 c.c. of 1.20 nitric acid are used to complete the solution and oxidize the iron. Boiling is continued two minutes longer and then 200 c.c. of water are introduced. From a small pipette a solution of permanganate of potassium is delivered, a little at a time, until a slight precipitate of manganese oxide is obtained that does not perceptibly dissolve after twenty minutes' boiling. The beaker is removed from the fire and, after a few moments, is placed in a tray of running water until cold. Its contents are filtered into a heavy suction flask through an asbestos filter using a 1¼-inch carbon filter tube, supporting the asbestos on a perforated porcelain plate.* (The asbestos is washed in nitro-hydrochloric acid and freed from chlorine test with distilled water before it is used.) The residue on the asbestos filter is washed fifteen times with 20 c.c. of 1 : 3 sulphuric acid diluted with 500 c.c. of water.

The filtrate and washings are returned to the 600 c.c. beaker together with 30 c.c. of dilute sulphuric acid, additional. The volume is now about 350 c.c. and titration is begun with a standard of double sulphate of iron and ammonia. The double sulphate standard is dropped in from a 100 c.c. burette until the fluid in the beaker loses all brown tints and assumes a practically colorless shade, in plain vanadium, or in vanadium steels containing less than 1 per cent of chromium. If much chromium is present, i.e., from 2 to 6 per cent, the iron sulphate is added until the chrome green no longer grows darker, and two or three c.c. more to insure an excess. There are two reasons why the sulphate standard should be added at the start. In the first place, though no chromium may have been added to the steel, there is often a little manganic oxide held in solution, or permanganate, which would reduce a portion of the sulphate standard. Again there is never any certainty that small amounts of chromium are not present. The quantity of sulphate standard required in the foregoing reduction should be noted in case the determination of chromium is part of the program. The permanganate of potassium standard is next dropped into the solution and, as soon as the pink color begins to disappear slowly, the standard is added three drops at a time, until a very faint pink color is obtained that persists after 30 seconds stirring. Should even as much as 5 or 6 per cent of chromium be present a practiced eye can easily detect pink reflections through the chrome green. These pink glints can be seen in the bottom of the beaker and, as one looks down through the mouth of the latter, a rounded bright spot is seen that takes on a pink flush when the permanganate is in excess.

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* Now use porous thimble 1$\frac{5}{16}$ inches outside diameter and 2 inches high, supported in a glass filter tube 1⅝ inches O. D. by 3¼ inches high. A piece of flat Gooch rubber tubing of 1¾-inch diameter is required to make the tight connection between the thimble and the glass filter tube. This arrangement does away with the use of an asbestos filter and requires very little water pressure for rapid filtration. The apparatus is shown in the photo on page 298.

Vanadium.—The solution is now ready for the titration of the vanadium, alone:* 0.6 c.c. of potassium ferricyanide is poured into the beaker with a convenient dropper, having an etched mark on it to indicate the 0.6 c.c., so that the same quantity of the indicator is always taken.† The ferricyanide imparts a brown tint to the iron solution. The ferrous ammonium sulphate standard is again dropped in, a little at a time, until one drop produces a green coloration that is *free* from yellow tints.‡ The titration is continued to a blue. The number of c.c. of double sulphate standard required in this second titration less the number needed to produce a similar shade in an imitation test, made with a steel that does not contain vanadium, gives the amount of the sulphate standard required to reduce the vanadic acid present. This remainder is multiplied by 2.54 to obtain the number of milligrams of vanadium in the sample. With each lot of analyses, two tests are made of plain steels to which have been added known weights of standard ferro-vanadium drillings or powder. If the usual operations recover the vanadium added all of the tests made at the time are accepted. The amount of double sulphate standard required by the blank tests on non-vanadium steels is deducted from all tests before making calculations. This deduction for plain vanadium or vanadium-chrome steels where the per cent of chromium is not much in excess of 3 per cent, varies from 0.4 to 0.9 c.c. This applies to a volume of approximately 350 c.c. An increased volume produces an increased blank. A test, in duplicate, for vanadium by the foregoing manipulations can be carried through in an hour and a half in the presence of chromium, nickel, tungsten or molybdenum.

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* Read pages 21 to 22.

† Five grams of potassium ferricyanide dissolved in 130 c.c. of water.

‡ Titrations are now all carried to a blue, i.e., until 3 drops of the double sulphate change the dark green to a distinct blue.

The presence of much chromium increases the blank somewhat. With no chromium present the blank is about 0.3 to 0.4 c.c. and, with chromium in the solution to the extent of 3 per cent, it is 0.4 to 0.9 c.c. With a chromium content of 4 per cent it is 1.0 to 1.2 c.c. It is always best to make control tests and blank tests, when high chromium and tungsten steels are being analyzed, with mixtures imitating closely the samples submitted for analysis. It is very important when dealing with alloy steels, containing large percentages of chromium and tungsten, to digest the drillings until the tungstic acid is a bright yellow before boiling with the excess of permanganate solution. One should, when the tungsten has "cleaned well," add permanganate until, after twenty minutes boiling, sufficient excess of manganese oxide is present to give the separated tungstic acid a chocolate color. Then proceed as usual.

When nickel is present in the steel in quantities ranging from 3 to 5 per cent the same method applies, but it must be borne in mind that, when ferricyanide of this concentration (5 grams in 130 c.c. of water) is used, in a few minutes, nickel ferricyanide separates, hence the titration must be proceeded with immediately.

Molybdenum does not interfere with the titration of vanadium, though the former element be present in large quantities.

Vanadium in Ferro-Vanadium.—*The determination of vanadium in ferro-vanadiums of the low silicon type offers no difficulties except that segregation is considerable. It is always advisable to make at least three tests of each sample and average the results. From 0.2 to 0.3 gram are taken and proceeded with exactly as in steels until the titration is to be made when, instead of adding the double sulphate standard first, the completeness of the oxidation of the ferro-vanadium is tested by adding three drops of the permanganate standard. If this gives a suggestion of pink to the solution, the ferricyanide indicator is added and then the ferrous sulphate standard until the light sky blue of the vanadyl salt is darkened *slightly* by the deeper blue caused by the excess of ferrous standard. This end-point is very satisfactory but requires a little experience on the part of the analyst. The amount of sulphate standard used is noted and then the permanganate standard is added, *at once*, until a *distinct* reddish pink color is obtained that does not fade perceptibly after thirty seconds vigorous stirring. This end-point might be described as an old rose shade. Blanks are run on the same weights of a plain carbon steel in exactly the same way and deducted from the amount of sulphate required to produce the blue and from the amount of permanganate required to restore a pink color. If less permanganate than sulphate is used, after correcting the sulphate reading to the permanganate basis, the presence of chromium is indicated and a qualitative test for the latter element can be made in an hour by fusing 0.8 gram of the ferro-vanadium with 10 grams of sodium carbonate mixed with 2 grams of nitrate of potassium. The melt is dissolved in water. The residue is removed by filtration in the cold. A yellow-tinted filtrate confirms the presence of chromium. Several tenths of 1 per cent of chromium are frequently present.

The amount of double sulphate should not be taken as a basis of percentage calculations unless it is positively known that chromium is absent. The sulphate should be first added as described. This should be immediately followed by the addition of the permanganate standard as given and the amount of the latter standard required to produce the permanent reddish pink should be multiplied by 2.54 to find the milligrams of vanadium in solution. For instance in 50 per cent ferro-vanadium it is not practical to take more than 0.4 gram for analysis. One c.c. of the double sulphate equals 0.00086 gram of chromium or only 0.215 per cent chromium, but it also equals 0.635 per cent vanadium, i.e., 0.2 per cent chromium would raise the vanadium content 0.6 per cent if not eliminated by calculating the vanadium from the permanganate used to obtain the old rose tint. When ferro-vanadium contains much silicon, about 4 per cent or more, the borings or powder may not dissolve completely in sulphuric and nitric acids. The following modification is necessary: Treat 0.3 to 0.6 gram of sample with 60 c.c. 1.20 nitric acid in a No. 5 porcelain evaporating dish. When heat produces no further action add 1 c.c. or more of hydrofluoric acid, which promptly gives a complete solution. 60 c.c. of 1 : 3 sulphuric acid are poured into the dish, the watch-glass is removed and the solution is evaporated to heavy fumes to remove the hydrofluoric acid. The sulphates are dissolved in water and transferred to a 600 c.c. beaker and the analysis completed as in low silicon ferro-vanadium.

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* Read pages 14 to 15.

Ferro-vanadiums containing from 0.5 to 6.0 per cent of copper present a slight obstacle. When the ferricyanide indicator is added copper quickly produces a light yellow cloud of copper ferricyanide that entirely prevents any end-point being seen. In such cases dissolve the ferro-vanadium in 1.20 nitric acid; evaporate dry; ignite; redissolve in HCl; dilute to 300 c.c. and pass H_2S until saturated; filter out the copper sulphide; wash it with H_2S water; evaporate filtrate to about 150 c.c.; add a few crystals of chlorate of potash to the not too concentrated solution (potassium chlorate explodes when heated with conc. H_2SO_4); evaporate to thick fumes; take up in water, heating until all is in solution; add 20 c.c. of 1.20 nitric acid; boil with $KMnO_4$ and finish the V as described.

As ferro-vanadium samples are, at times, quite variable it is always best to make several tests of the latter and report an average of the results obtained. If the copper content does not exceed 0.3 to 0.4 per cent, even when 2 grams of sample are taken, the vanadium can be titrated before the clouding begins if it is proceeded with as quickly as possible after the addition of the ferricyanide.

Small Amounts of Vanadium.*—For the determination of small amounts of vanadium, ranging from 0.02 to 0.05 per cent, it is expedient to dissolve from 6 to 8 grams of the steel for analysis. Such large weights of steel are treated first with 60 c.c. of 1 : 3 sulphuric acid and 100 c.c. of water. When this action is over, 120 c.c. of 1.20 nitric acid are added to complete the solution and to oxidize the iron. Then continue the analysis as usual. Blanks should be carried along with equally large amounts of a plain carbon non-vanadium steel. The writer would advise caution in the use of manganese sulphate to discharge any persistent pink color when boiling with permanganate, as its use in large amounts seems to increase blanks, apparently causing part of the permanganate to pass into solution in the manganic condition. Even the blank filtrates have a brown tint as though containing a few hundredths of 1 per cent of chromium. This would seem, in a measure, similar to the solution of iron hydrate in iron salts. On discontinuing the use of an excessive quantity of the manganese sulphate, lower and more uniform blanks and freedom from brown tints therein were attained. Do not add over 0.200 gram $MnSO_4$.

If pink colorations occur due to excessive additions of the permanganate, dilute further with distilled water and a drop or two of ferrous sulphate and boil until they are destroyed. It is rare that distilled water does not contain enough traces of organic matter to accomplish this purpose. (A pink color in the analysis of ferro-vanadium does no harm in the determination of vanadium as the sulphate standard is added at the start; and the vanadium is calculated from the amount of permanganate required to produce an old rose shade, after getting the blue with the sulphate standard and ferricyanide indicator.)†

Chromium, as already intimated, can be determined in the presence of vanadium and in the same operation.

In steels, the amount of double sulphate used to discharge all red colorations, leaving the solution a clear light green, free of all yellowish tints, less the number of c.c. of the permanganate standard required to produce a slight permanent pink

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[*] See the author's new method for determination of large and small amounts of Cr, V, Al, U, Ti, and Zr by removing the bulk of the ferrous iron with ammonia. Pages 30 and 31.

† Read pages 14-15.

reflection, thereafter, equals the amount of double sulphate necessary to reduce the chromic acid present to chromic sulphate. One c.c. of the double sulphate usually equals 0.00087 gram of chromium. As already explained, the ferricyanide indicator is now dropped in, and the sulphate standard again follows until three drops of it produce a blue.[*] The amount of sulphate consumed by this last titration is equivalent to the vanadic acid present, after deducting the regular blank, which is usually 0.1 to 1.0 c.c., depending on the amount of chromium. A sample calculation is given as an illustration. (2 grams are taken for analysis.)

FIRST PART OF THE TITRATION TO OBTAIN THE CHROMIUM (MADE BEFORE ADDING FERRICYANIDE)

$KMnO_4$		Double Sulphate
9.1 c.c.	second reading of burette	28.6 c.c.
2.3 c.c.	first reading of burette	12.4 c.c.
6.8 c.c.		16.2 c.c.

Calculation

16.2
6.8

9.4 c.c. equal sulphate used by chromium
$9.4 \times 0.00087 \times 100 \div 2 = 0.4089$, or per cent chromium.

SECOND PART OF THE TITRATION (MADE IMMEDIATELY AFTER ADDING THE FERRICYANIDE INDICATOR) TO OBTAIN THE VANADIUM

Sulphate

31.4 c.c. second reading of burette.
28.6 c.c. first reading of burette

2.8 c.c.
0.4 c.c. equals regular vanadium blank for low per cent chromium

2.4 c.c.

Since 1 c.c. of sulphate equals 1 c.c. of permanganate or 0.00251 gram of vanadium, therefore $2.4 \times 0.00254 \times 100 \div 2 =$ 0.305 per cent vanadium.

Small Amounts of Chromium in Ferro-vanadium.—Ferro-vanadium frequently, as stated, contains one or two tenths of a per cent of chromium. The most satisfactory way to estimate these small amounts, in the presence of large per cents of vanadium, is to fuse 1 gram of the finely ground powder or thin drillings with 20 grams of sodium carbonate and 4 grams of niter. After the fusion is quiet, keep it molten for thirty minutes. Dissolve the melt in as little water as possible in a platinum or porcelain dish. Add pulp; filter; wash with sodium carbonate water. Evaporate the filtrate and washings to about 40 c.c. If the solution is not clear, add a little pulp, filter and wash again. The filtrate and washings should not exceed 40 to 50 c.c. if the chromium content is only a tenth of a per cent or thereabout. Compare this solution with a standard consisting of 0.070 gram of c.p. potassium dichromate made slightly alkaline with sodium carbonate and diluted to 250 c.c. in a volumetric flask. It is made alkaline by adding sodium carbonate until the red color of the dichromate has all been converted into the yellow of the sodium chromate. 1 c.c. equals 0.0001 gram of chromium. Use the same comparison tubes as described under the color method for titanium. Rinse one of the tubes three times with some of the standard. Then pour into it exactly 10 c.c. of the standard solution. If the chromium content is about 0.20 per cent, the standard will be yellower than the test. Add water to the standard, 1 to 2 c.c. at a time, until its color is only slightly stronger than that of the test. Continue the addition of water in $\frac{1}{2}$ c.c. amounts until the standard is just turned lighter than the test. Suppose the standard matches the test in color at 27.5 c.c. and the volume of the test is 59.5 c.c. This gives the proportion:

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[*] The sulphate standard is now added until three drops of it change the dark green to a blue.

$$\begin{array}{ccccccc} \text{Standard Vol} & : & \text{Test Vol} & & \text{10 c c Std} & & \\ 27.5 & : & 59.5 & :: & 0.001 & : & X \end{array}$$

$5.95 \div 27.5 = 0.21$ or 0.21 per cent chromium.

Standardizations.—The writer prefers to standardize permanganate of potassium against recrystallized oxalic acid kept in tightly stoppered bottles:* 1.58 grams of potassium permanganate are dissolved in a liter flask with distilled water and diluted to the mark. 19.5815 grams of double sulphate of iron and ammonia, i.e., $FeSO_4 \cdot (NH_4)_2SO_4 + 6\,H_2O$, are dissolved in the same manner, with the addition of 50 c.c. of 1 : 3 sulphuric acid, and diluted to one liter. Usually the relationship between these two standards is that from 40.2 to 40.5 c.c. of the permanganate equal 40 c.c. of the double sulphate. The vanadium value of the permanganate standard is checked against the oxalic acid, and the vanadium value of the sulphate standard is calculated from its relation to the permanganate standard.

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* Keep oxalic acid in a cool place to prevent loss of water of crystallization.

*The 1.58 grams of permanganate solution, theoretically, should be equivalent to 2.56 grams of vanadium. Its actual value is found as follows: 0.1424 gram of oxalic acid is dissolved in about 100 c.c. of water plus 20 c.c. of 1 : 3 sulphuric acid and heated to 80° C. The permanganate standard is then added until one drop produces a permanent pink. This usually requires 45.45 c.c. of the permanganate. We in the first place have the proportion:

Oxalic Acid		Permanganate				
63	:	31.6	: :	0.1424	:	X

This gives X equals 0.07142, or 0.07142 gram of pure permanganate will oxidize 0.1424 gram of oxalic acid. By the above titration it is found that it requires 45.45 c.c. of the permanganate standard to oxidize 0.1424 gram of oxalic acid. Therefore each c.c. of the permanganate standard must contain 0.07142 divided by 45.45, or 0.001571 gram of 100 per cent potassium permanganate. We thus obtain the final proportion, or

$$1.58 : 2.56 :: 0.001571 : X$$

X equals 0.002545, or 1 c.c. permanganate solution equals 0.002545 gram of vanadium.

The chromium value of these standards is found by adding to 2 grams of a plain carbon steel a weighed amount of recrystallized potassium dichromate. This mixture is put through the entire process of an analysis. Taking the percentage of chromium in dichromate of potash as 35.35 per cent, the sulphate standard is found to have a value that varies from 0.00085 to 0.00087 gram of chromium per c.c.

It must be constantly borne in mind that to attain success in vanadium and chromium titrations in steels, it is absolutely essential when coming back with permanganate to stop with the first 3 drops that give a faint pink reflection that is still faintly, but distinctly, visible after *thirty seconds* stirring.

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* Read pages 19 to 20.

Furthermore, the next step is to add the ferricyanide indicator. Then the ferrous ammonium sulphate is quickly added until 3 drops produce the first distinct darkening of the green to a distinct blue. Do not continue to add the sulphate to a still darker blue. In short, if the pink end-point is overdone, and then the blue one also, the error is doubled. Always aim to finish standards, blanks and tests exactly as described.

THE TITRATION OF VANADIUM IN FERRO-VANADIUM AND PLAIN VANADIUM STEEL, AVOIDING THE INTERFERENCE OF SMALL AMOUNTS OF MANGANIC OXIDE, PERMANGANATE AND CHROMATE IN THE SOLUTION

During four or more years subsequent practice of the vanadium method, given in the preceding pages of Chapter II, some changes have been made to avoid the interference of any small amounts of manganese present in the solution, in the manganic state; or chromium that may be in the sample to the extent of 0.20 to 0.10 per cent, or less; or of uranium. The latter element, when in the solution to the amount of several per cent, forms objectionable brown tints, seriously obscuring the end-point if the ferricyanide indicator is added first; then the sulphate standard; and then the permanganate standard to obtain the old rose shade. Before this end-point is attained, the uranium brown color has overshadowed it. By the following modification these interferences are avoided.

First from a 100 c.c. burette deliver into an 800 c.c. beaker 40 c.c. of the sulphate standard. Also pour in the beaker 350 c.c. of distilled water and 30 c.c. of 1 : 3 sulphuric acid. Titrate this mixture with the permanganate standard to get the relation between the two standards; assuming the vanadium value of the permanganate as correct, that of the sulphate is calculated from the result of this titration. The standards prepared as given on pages 12 and 13 should be nearly equivalent in vanadium value.

Ferro-vanadium.—Now, instead of adding the ferricyanide indicator at the start, the titration is begun by adding the sulphate standard until all brown or pink tints are gone and a green color begins to appear due to the partial reduction of the vanadic acid to the hypovanadic state. Next, add the permanganate standard with continued stirring until a strong reddish pink is reached; stir well and wait thirty seconds to insure a complete reaction between the vanadium and the permanganate as the former acts rather slowly at room temperature, make sure that the red color does not fade perceptibly during the pause In case a fading is noted more permanganate must be added, followed by more stirring, and so on, until the fading is no longer noticeable. However, such fading does not occur as a rule more than once, if the red end-point is approached rather slowly and with much stirring after each addition of the permanganate standard.

The sulphate standard is, again, dropped in to remove the excess of the permanganate; this is accomplished by adding, the former standard, a few drops at a time, until the deep red is all gone and the solution has taken on, in the main, a yellow tint with a very slight but distinct tan shade in it. At this stage 2 drops of the permanganate should cause a reappearance of a slight suggestion of pink, as one looks down through the mouth of the beaker. The operator can then discharge this very faint pink with 2 drops of the sulphate standard. The solution is now ready for the titration proper. The reading of the sulphate burette is noted; the ferricyanide indicator is poured in, and the sulphate standard is dropped in immediately thereafter, until the green color that forms is changed to the *first* deep blue. This dark blue is the end-point, and should be rather rapidly approached to catch the first change from the dark green to the blue. Of course the solution is stirred vigorously during the titration. The sulphate used for this last titration, i.e., subsequent to the pouring in of the indicator, minus the blank, is the sulphate equivalent of the vanadium.

Plain Vanadium Steel.—With a vanadium content of 0.10 to 0.30 per cent, take from 4 or 5 grams of sample and proceed as described for chrome vanadium steel on page 18, using 50 c.c. of 1 : 3 sulphuric acid to effect the solution of the drillings, diluting with about 20 c.c. of water to prevent the formation of crusts of sulphate of iron; warm until no further evolution of fine bubbles of hydrogen is visible; and then add 60 c.c. of 1.20 nitric acid to oxidize the ferrous iron; heat until all red fumes are gone; proceed further as given on page 18, except that the excess of the hydrated oxide of manganese is filtered out by means of a porous thimble, avoiding entirely the use of asbestos filters. This same filter is now used for this purpose in the analysis of ferro-vanadium. But very slight suction is required. (See photo 20, page 298.)

The filtrate and washings can be pink with an excess of permanganate as will be seen. The volume of all tests and blanks should be the same and should not exceed 350 c.c. just before the titration. Titrate the above filtrate in the same manner as given for the ferro-vanadium, i.e., discharge all pink or brown tints to a clear greenish yellow (of course the green is not so noticeable in steels as it is in ferro-vanadium) by adding, at the start, about 10 or more c.c. of the sulphate standard; then continue as in the ferro and calculate the vanadium from the sulphate required to produce the dark blue after the addition of the indicator, less the blank, which for this procedure is, in this laboratory, from 0.8 to 0.9 c.c. for plain vanadium steels.

Blank Tests.—To obtain the blank test to apply in the analysis of ferro-vanadium of from 30 to 40 per cent vanadium, dissolve 200 mgs. of plain carbon steel; and for plain vanadium steels, dissolve 5 grams of plain steel, just as directed for ferro-vanadium and plain vanadium steel, respectively. Put these blanks through all of the operations and titrations, noting the amount of sulphate required to produce a dark blue after the ferricyanide indicator has been added in the order given. The portion of a c.c. so consumed constitutes the blank to be deducted from all tests. Pay no attention should the dark blue of the blank begin to fade in a few minutes. This is caused by the oxidizing action of the nitric acid left in the solution. In actual work containing vanadium, the blue end-point does not fade or change so quickly.

Blanks can also be determined by difference, i.e., a known amount of vanadium is added to a plain steel and it is then analyzed for vanadium. Assume, for example, that the value of the sulphate standard is 1 c.c. equals 0.00254 gram vanadium; further, that to 4 or 5 grams of plain steel have been added 30 mgs. of ferro-vanadium containing 38.23 per cent vanadium. This mixture is then analyzed for vanadium and is found to consume 5.3 c c. of the standard sulphate. Now 0.3823×30 equals 11.469 mgs. of vanadium and should require, if there were no blank, 11.469 divided by 2.54 equals 4.51 c.c.; therefore the blank is 5.3 less 4.51 or 0.79 c.c., or the blank to be deducted from all titrations to get the number of c.c. of sulphate consumed by the vanadium alone.

Chrome Vanadium Steels.—These steels are titrated as given on pages 5, 6, 7, and 10. On page 6 the directions read to completely reduce the chromium in the solution by adding the sulphate standard until the "chrome green no longer grows darker (that is, the green shade no longer gains intensity) and 2 or 3 c.c. more to insure excess." The following example shows how the operator can be sure that he has an excess of the sulphate and that, therefore, no chromium remains in the chromic acid state which would consume some of the sulphate standard and be counted as vanadium. This example is particularly useful when steels high in vanadium are to be dealt with, i.e., containing from 0.50 to 2.00 per cent vanadium and over:

EXAMPLE

FIRST PART OF THE TITRATION TO OBTAIN THE CHROMIUM (MADE BEFORE ADDING THE FERRICYANIDE)

$KMnO_4$		Double Sulphate.
21 c.c.	second reading of the burette	97 2 c.c.
9 c.c.	first reading of the burette	0 2 c.c.
12 c.c. (A)		97 0 c.c.
		12 0 (A)
		85 0 c.c.

85.0×0.00085×100 divided by 2 equals 3 61 per cent chromium when 2 grams are taken.

SECOND PART OF THE TITRATION TO OBTAIN THE VANADIUM PERCENTAGE (MADE IMMEDIATELY AFTER ADDING THE FERRICYANIDE INDICATOR)

Sulphate Used by the Vanadium

8 2 c.c. second reading of the burette.
1 2 c.c first reading of the burette.

7 0 c.c. or (B)
0 8 c.c (blank)

6.2 c.c. 6.2×0.00254×100 divided by 2 equals 0.78 per cent V.

(A) should always be several c.c. in excess of (B) to insure no chromium being dragged over into the second part of the titration in the unreduced state and counted as vanadium.

THE TITRATION OF CHROME VANADIUM STEELS IN A MANNER SIMILAR TO FERRO-VANADIUM

In this laboratory these steels are now frequently titrated for vanadium by oxidizing back the vanadium (after the usual excess of the double sulphate has been dropped in the manner just described to reduce both the Cr and V) by adding the permanganate standard until a strong pink is obtained. The solution is then stirred for a half minute vigorously to note if there is a perceptible fading of the permanganate. If there is a noticeable fading, then more permanganate is added to again obtain a strong pink, which must show no perceptible change after thirty seconds' further stirring. Then the excess of permanganate is slowly, drop by drop, taken up by adding, with prolonged stirring, the sulphate standard until two drops leave only the faintest suggestion of a pink as one looks down through the solution. When the right point is reached, two drops of the permanganate should again give a distinct increase of the pink shade, even after the prescribed amount of stirring. Two drops of the sulphate standard should reduce this pink again to a faint color. The solution can be thus adjusted back and forth to suit the operator, to a nicety. It is then ready for the addition of the indicator and the final titration to obtain the number of c.c. used by the blank plus the vanadium, or (B).

THE DETERMINATION OF THE CHROMIUM VALUE OF THE DOUBLE SULPHATE, AND THE VANADIUM BLANK FOR CHROMIUM VANADIUM STEELS BY MEANS OF A KNOWN MIXTURE.

Suppose the above values are needed for a steel of about 3 or 4 per cent chromium and 0.50 to 1.00 per cent vanadium; then a suitable mixture would be 2 grams of plain carbon steel, free from vanadium, 170 milligrams of c.p. crystals of potassium dichromate and 0.075 gram of ferro-vanadium of 21.8 per cent V. The analytical data obtained in this particular case, after putting the mixture through the regular operations given in the foregoing pages, are found below, together with the calculations:

$KMnO_4$ used in the first part of the titration to obtain the chromium value		The double sulphate used by the chromium, etc
65.8 c.c.		81.0 c.c.
56.2 c.c.		00.4 c.c.
9.6 c.c.		80.6 c.c.

80.6 c.c.
9.6 c.c.

71.0 c.c. used by the chromium, alone.

Potassium dichromate contains 35.35 per cent chromium; therefore 0.170×0.3535 divided by 71.0 equals 0.000847, or 1 c.c. of the double sulphate equals 0.000847 gram of chromium.

The second part of the titration made immediately after adding the ferricyanide indicator gave the following readings of the sulphate consumed by the vanadic acid in the solution:

88.2 c.c. second reading of burette
81.0 c.c. first reading of burette

7.2 c.c. sulphate used by V_2O_5 and the blank.

0.075×0.218 equals 0.01635 gram of vanadium added. Taking the vanadium value of the sulphate standard as found by standardizing it against sodium oxalate, as given on page 20, or 1 c.c equals 0.002536 gram of vanadium, one obtains by dividing the vanadium added, or 0.01635, by 0.002536 a quotient of 6.4; hence 7.2 c.c. minus 6.4 c.c. equals 0.8 c.c. or the sulphate blank to be deducted from the total amount of sulphate consumed in the vanadium titration of the above range of chrome vanadium steels.

THE STANDARDIZATION OF THE DOUBLE SULPHATE FOR VANADIUM BY SODIUM OXALATE

(A) The strength of the standards per liter are the same as given on page 12. 150 mgs. of c.p. sodium oxalate prepared according to Sorensen are weighed into a beaker, and dissolved in 20 c.c. of 1 : 3 sulphuric acid plus 150 c.c. of distilled water. (This sodium oxalate can be obtained for a small fee from the Bureau of Standards at Washington, D. C., or can be prepared by recrystallizing the c.p. salt offered by the dealers.) The mixture of sodium oxalate is heated to about 80° C. and titrated with the permanganate standard solution until one drop of the same changes the mixture to the faintest pink.

(B) Also a measured amount of the permanganate standard is placed in a beaker together with 20 c.c. of 1 : 3 sulphuric acid and titrated with the double sulphate standard until the pink color just disappears to get the ratio between the two standards. ($10\ FeSO_4+2\ KMnO_4+8H_2SO_4=5\ Fe_2(SO_4)_3+8\ H_2O+K_2SO_4+2\ MnSO_4$.) The following equation explains the reaction occurring in (A):

$$2KMnO_4+5Na_2C_2O_4+13H_2SO_4=K_2SO_4+2MnSO_4+10NaHSO_4+8H_2O+10CO_2. \quad \text{(1)}$$

Equation (2) shows the relation between the potassium permanganate and vanadium:

$$5(VO)_2(SO_4)_2+2KMnO_4+8H_2SO_4=5(VO)_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O. \quad \text{(2)}$$

Equation (1) shows that $2KMnO_4$ are equivalent to $5Na_2C_2O_4$.

Equation (2) shows that $2KMnO_4$ are equivalent to 10V; therefore

$$\underset{(670)}{5Na_2C_2O_4} \text{ are equivalent to } \underset{(510)}{10V}.$$

The following proportion will hence give the vanadium equivalent of 0.150 gram of sodium oxalate:

$$670 : 510 :: 0.150 : X.$$
$X=0.11417$ gram of vanadium.

By titration (A) it was found that 45.35 c.c. were required of the permanganate standard to combine with 0.150 gram of oxalate so that 1 c.c. of the permanganate equals 0.11417 divided by 45.35, or 0.002517 gram of vanadium. By titration (B) it was found that 40 c.c. of the sulphate were equivalent to 40.3 of the permanganate; therefore 1 c.c. of the double sulphate equals 0.002517×40.3 divided by 40, or 0.002536 gram of vanadium. The double sulphate standard should be tested according to (B) on each occasion that it is used and its vanadium value adjusted according to the relation so found.

SOME RECENT ANALYSES OF FERRO-VANADIUM

	No 1	No 2	No 3	No 4	No 5
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
C	0.06	0.05	0.08	0.13	0.19
Mn	0.14	0.18	0.19	0.22	4.11
Si	1.52	0.97	0.66	0.92	8.35
V	40.41	40.54	39.40	39.50	35.62
Ni	0.72	1.32	1.68	2.50	7.74
Cu	None	None	None		None
Al	0.95	1.22	1.33	0.92	1.43
Mo	0.92	1.00	0.92	0.60	
Fe	54.65	54.10	55.20	54.50	42.60
P				0.13	
S				0.65	0.20

For the determination of Vanadium in Vanadium Ores, see page 369.

CHROMIUM AND VANADIUM IN ALLOY STEELS

The Method as it is Now Used by the Author for Routine Work.—Dissolve 3 grams of sample in 600 c.c. beaker; add 30 c.c. H_2SO_4 (1 : 3) and 700 c.c. water, and heat gently until dissolved. Add cautiously 30 c.c. HNO_3 (1.20 sp. gr.), increase heat slightly and boil until all brown fumes have been expelled. The tungstic acid of high speed steels changes from a dirty black to a yellow color when fully oxidized at this stage. The tungsten must show as a bright yellow residue or Cr and V results will be low. If not bright yellow, add more nitric and continue to digest until clean bright yellow tungstic oxide is obtained. Keep barely at boiling temperature till clean yellow.

Dilute with water to 300 c.c. volume; bring to a boil; add $KMnO_4$ solution (25 grams per liter) from a pipette or glass tube until a slight precipitate of manganese oxide begins to form. Boil for fifteen minutes to decompose any excess $KMnO_4$. Should the solution clear up on boiling, more $KMnO_4$ solution is added until a permanent precipitate forms that settles out, leaving the total sediment of a brown color even when tungsten is present. Cool to room temperature in a pan of cold running water; filter through a porous crucible, using suction, and wash residue in crucible fifteen times with water.

Clean the original beaker by rinsing with a few c.c. of ferrous sulphate, then with water to remove the sulphate. If there is a yellow deposit of tungstic acid adhering to beaker, use ammonia to dissolve, then rinse with water. Reject the cleanings. Transfer filtrate to original beaker; if perfectly clear, proceed with titration, otherwise refilter. Several tests may be filtered successively through the same porous crucible, until slowness of filtration warrants cleaning out the deposit.

Titration.—Solutions required: N/20 ferrous ammonium sulphate; N/20 potassium-permanganate; K_3FeCN_6 (5 grams 120 c.c. water).

Using two 100 c.c. burettes, graduated either in fifths or tenths of a cubic centimeter fill one with $KMnO_4$ and the other with N/20 FeAm sulphate, being careful to exclude all air bubbles.

Record readings of burettes, which should for convenience be zero or thereabouts. While continuously stirring test, add rapidly from burette, N/20 FeAm sulphate. The test passes through a gradual color change from yellow to green or perhaps a bluish tint, if considerable vanadium is present.

With a little experience, the operator may easily judge when no further change in color is caused by the addition of a few cc. in excess of the FeAm sulphate solution. At this stage all chromium is reduced to Cr_2O_3 and all vanadium to V_2O_4. Back titrate with N/20 $KMnO_4$ until just the faintest pink persists on stirring two minutes. The eye can be readily trained to observe a pink tinge in such a solution due to 1 or 2 drops of N/20 $KMnO_4$. At this stage all vanadium has been oxidized back to V_2O_5 and the excess FeAm sulphate destroyed with an equivalent of $KMnO_4$. By subtracting the c.c. of $KMnO_4$ consumed in back titration, from the total c.c. of FeAm sulphate used, we have the exact amount of sulphate solution required to reduce the chromium present. See "Calculations."

VANADIUM TITRATION

Having recorded the final burette reading in the chromium determination, transfer the last sulphate reading to a space set aside for calculation of vanadium—thus making it the starting-point for this determination. If less than 15 c.c. FeAm sulph. are left in the burette after the chromium determination, refill and note the reading before starting the vanadium titration, as it is bad practice to refill the burette in the midst of titration of the vanadium. Add from a pipette or glass tube, ½ c.c. K_3FeCN_6 solution and titrate rapidly yet carefully to the first appearance of a dark-blue color.

Note the burette reading and subtract the previous reading from it. A blank representing the amount of FeAm sulph. required to produce the blue end-point in the vanadium titration is further subtracted; this final difference is the exact amount of sulphate required to reduce the V_2O_5 to V_2O_4.

Standards, Duplicates, Precautions, etc. Do not filter warm or hot solutions through porous crucibles, because of the invariable tendency to reduce the chromium, thus giving a final value too low in per cent chromium.

When vanadium is present, the pink of the $KMnO_4$ used in back titration fades out on stirring and is not permanent until all V_2O_4 has been oxidized to V_2O_5. It is essential that the number of c.c. of $KMnO_4$ consumed in back titration of the chromium be in excess of the number of c.c. of sulphate used in the vanadium titration to the extent of 3 or 4 c.c. at least. Otherwise a little chromium may escape reduction and be counted as vanadium. This is important.

Should the operator observe that in back titrating for chromium only a few c.c. give a permanent pink; stop; add FeAm sulph. until test is green, then resume the $KMnO_4$ back titration.

The following synthetic standard is suitable and convenient for chromium-vanadium steel.

$$\left.\begin{array}{c} \text{200 mg } K_2Cr_2O_7 \text{ (35.35 per cent Cr)} \\ \text{40 mg. FeV (38.35 per cent V)} \\ \text{2 grams plain steel} \end{array}\right\} \begin{array}{c} \text{3.51 per cent Cr} \\ \text{.765 per cent V} \end{array}$$

The plain steel used in making the standard analysis contains .003 per cent Cr and no vanadium.

If a test clouds up immediately on putting in the ferricyanide solution for the vanadium determination, copper in considerable quantity is present.

Nickel and cobalt up to 5 per cent do not interfere if the vanadium titration is made rapidly, after putting in the ferricyanide; the test clouds on standing for some time.

If copper is present in sufficient quantity to give a dense cloud when the K_3FeCN_6 is added, then dissolve the steel as already described, using the precautions given to insure prefect solution if tungsten be present.

Then filter off the tungsten, if any be present; wash it with dilute sulphuric acid wash water; evaporate filtrate and washings to slight fumes of SO_3. Dense fuming renders the chromium insoluble.

Add 200 c.c. of water and 20 c.c. more of 1 : 3 sulphuric acid; heat until all salts are in solution and pass a rapid stream of H_2S through the solution until precipitate settles out well and supernatant solution is clarified. Filter into 500 c.c. beakers, wash twenty-five times with H_2S water ($\frac{1}{2}$ c.c. H_2SO_4 (1 : 3), 500 c.c. water, saturated with H_2S). Concentrate filtrate to 100 c.c. volume, add 30 c.c. HNO_3 (1.20), boil for five minutes, dilute to 300 c.c., bring to a boil, add a slight excess of permanganate, boil, and proceed in the usual manner for determining chromium and vanadium. The CuS precipitate is quantitative and may be determined by titration with KCN. It is a rare occurrence that enough copper is present to interfere.

EXAMPLES

$K_2Cr_2O_7$ 200 mg.
N/20 $KMnO_4$ FeV . 40 mg. N/20 FeAm sulph.
11 8 .Plain steel....... 2 gm. 96 0
0 0 0 0
11.8 c c. 96 0
−11 8
84 2 c.c.
.3535 gm. Cr in 1 gm. $K_2Cr_2O_7$
2
84.2).07070000(0008396 7 0
X 100 0 0
7 0
1 c.c. = .084 per cent Cr on 1 gm. basis −6 0
V-blank 1 0 c.c.
.3825 gm. V in steel
04
.0153000(00254 gm. = vanadium value at 1 c.c. FeAm sulph.
1524 6 02 c.c. = FeAm sulph to reduce vanadium added.
600
508
1 c.c. = .254 per cent V on 1 gm. basis.

Method Used in Cr and V

N/20.$KMnO_4$	Alva Std 3 gm	N/20 FeAm sulph.
21 0	1 03 per cent Cr	53 0
11 8	228 per cent V	7 0
9 2 c.c.		46 0
		9 2
		36 8 c.c.

0103 gm Cr .n 1 gm. Alva.
3
36 8) 030900(00084
2944
1460
1472

56 7
53 0
3 7
2 7
V-blank 1 0 c.c.

1 c c. = 084 per cent Cr on 1 gm basis.

.00228 gm. V in 1 gm Alva
3
.006840(00254 gm V value of 1 c.c. N/20 FeAm sulph.
508 2 7 c c
1760

N/20 $KMnO_4$	No 30a 1 gm	N 20 FeAm sulph	
31 0	49	59 0	
21 0	084	0 0	63 5
10.0 c.c.	196	59 0	59 0
	392	10 0	1 5
	4)4 116	19 0 c c.	1 0 c c blank
	1 029		3 5
		X	254
			1270
			762
			4) 8890
			222

1 03 Cr
22 V

	No 30_2 3 gm	
39 1	12 3	45 0
31 0	084	0 0
8.1	492	45 0
	984	8 1
		3)36 9
	1 0332	12.3 c c.

1.03 Cr	48.6
.22 V	45.0
	3.6
	1.0 c.c. blank
	2.6
	X 254
	1524
	508
	3) 6604
	22

Variation from the above Directions

.5 per cent Cr to 2 per cent Cr	use 3 to 5 gm. samples
2 per cent Cr to 5 per cent Cr	use 1½ to 2 gm. samples
Over 5 per cent Cr	use 1 gm.

When 5-gram samples are taken, dissolve in 40 c.c. H_2SO_4 (1 : 3) and 60 c.c. distilled water, then oxidize with 40 c.c. HNO_3 (1.20), after which proceed as outlined in the foregoing method.

Rapid Method for Preliminary Bath Tests

$KMnO_4$ Method, Destroying Excess Pink Coloration with Manganese Sulphate: Chromium, 35 Minutes. Weigh 2 grams sample in 600 c.c. beaker, dissolve in 100 c.c. H_2SO_4 (7½ per cent by vol.) on stove or hot plate. When dissolved, remove from heat and add cautiously 30 c.c. HNO_3 (1.20). Replace on stove and boil off all brown fumes. Dilute to 200 c.c. with boiling distilled water.

Add $KMnO_4$ solution (25 grams per liter) to the boiling solution in small doses until test is pink, and a slight cloudiness persists. Boil five minutes; remove from stove; add cautiously 200 mg. manganese sulphate crystals; replace on stove and boil five minutes longer to destroy excess $KMnO_4$. Place beaker containing test in a pan of cold running water and bring to room temperature.

Filter test through a porous clay crucible, wash ten times with distilled water from fine jet, transfer to original beaker, then titrate with N/20 FeAm sulph. and N/20 $KMnO_4$ in the usual manner.

EXAMPLE

KMnO$_4$	No 13 Std (70 Cr) 2 gm	**FeAm sulph.**
13 3	last reading	32.8
6	first reading	3 1
		29 7
12 7 to be subtracted from FeAm sulph.		12 7
		17.0 c c.

70 Cr in Std.
2 gm taken
17 c.c.)1 10000(08235
1 36

Factor

1 c c =.0824 per cent Cr in 1 gm. sample

KMnO$_4$	Sample No E-58 2 gm	**FeAm sulph.**
16 9		48 1
13 3		32 8
3 6 c.c.		15 6
		3 6
		12 0 c c

0824 Factor
12
1648
824
2 gm 9888
4944 .49 Cr

(Time required, 35 minutes.)

Remarks

100 c c. H_2SO_4 (7½ per cent = (30 c.c. H_2SO_4 (1 : 3))
(70 c c. water)

Moderate suction is used when filtering test through the porous clay crucible. Should test have a pink color after transferring to original beaker, add 100 mg. more of manganese sulphate and boil until cloud forms, requires about five minutes' boiling.

Cool; filter; then proceed with titration. *Do not increase the dose of manganese sulphate, as it makes the result too high (see page 28).*

EFFECT OF MANGANOUS SULPHATE ON CHROMIUM RESULTS

No. 13 Std. 2 gm. plus 100 mg Mn sulph.........	.69	correct
No. 13 Std. 2 gm. plus 200 mg Mn sulph.........	.71	correct
No. 13 Std. 2 gm. plus 500 mg Mn sulph.........	73	too high
No. 13 Std. 2 gm. plus 500 mg. Mn sulph....... .	76	too high
No. 13 Std. 2 gm plus 500 mg Mn sulph.........	773	too high
Correct chrome value for No. 13 Std..............	.70	per cent Cr

Modified Persulphate Method for Rapid Preliminary Bath Tests—Chromium—Time Twenty-five Minutes.—Weigh 1 gram sample in 400 c.c. beaker; dissolve in 100 c.c. H_2SO_4 (7½ per cent by volume). Add 30 c.c. HNO_3 (1.20) and boil until all brown fumes have been expelled. Add 20 c.c. $AgNO_3$ solution (6 grams per 1000 c.c. water) followed immediately by 20 c.c. ammonium persulphate solution (240 grams per 1000 c.c. water); then boil moderately until fine bubbles are no longer expelled.

Add 3 c.c. of a 5 per cent solution of HCl, and boil for two minutes; if solution has any trace of red color left, add 1 c.c. more of the 5 per cent HCl and boil another minute (i.e., the permanganate pink of the test should be destroyed with the smallest possible excess of HCl).

Cool in a pan of water to room temperature, then titrate with N 20 ferrous ammonium sulphate and N/20 $KMnO_4$ in the usual manner for chromium and vanadium, using a 5 per cent solution of K_3FeCN_6 as an internal indicator in the vanadium titration.

Remarks.—The chrome factor is a little higher and the vanadium blank lower in this method, as compared with the permanganate method filtering through clay crucible method.

EXAMPLE

$KMnO_4$	No 13 Std (70 Cr) 1 gm	FeAm sulph.
32 4		23.1
26 3		8 7
6.1	0843	14.4
	8.3) 70000	6 1
	664	8.3
	360	
	332	
	280	
	249	

$KMnO_4$		E-58 1 gm.	Fe Am Sulph
37 4			33 8
32 4			23 1
5.0			10.7
	0813		5 0
	5 7		5.7
	5901		
	4215		
	48051	48 Cr	

(Time required, 25 minutes.)

CHROMIUM AND VANADIUM (PRESENCE OR ABSENCE OF TUNGSTEN)

Persulphate Method.—Walters' Method, Combined with Author's Internal Indicator Scheme.—Weigh 1 to 2 grams in 600 c.c. beaker. Do not use more than 1 gram of sample if the chromium is above 3 per cent. Dissolve in 100 c.c. H_2SO_4 (7½ per cent by volume) on stove or hot plate. Add 30 c.c. HNO_3 (1.20 sp. gr.) and boil gently until all brown fumes have been expelled and tungsten has become bright yellow, if present. Dilute to 200 c.c. with distilled water, bring to boil, add 20 c.c. $AgNO_3$ solution (6 grams per 1000 c.c. water) followed immediately by 20 c.c. ammonium persulphate solution (240 grams per 1000 c.c. water); then boil gently until fine bubbles are no longer expelled.

Add 3 c.c. of a 5 per cent solution of HCl and boil for two minutes; if the solution has any trace of red color left, repeat the dose of 5 per cent HCl, and boil again (i.e., the permanganate pink of the test should be destroyed with the smallest possible excess of HCl). Cool in a pan of water to room temperature, then titrate (without filtering off any precipitates) with N/20 ferrous ammonium sulphate and N/20 $KMnO_4$ in the usual manner for chromium and vanadium, using a 5 per cent solution of $K{\cdot}FeCN_6$ as an internal indicator in the vanadium titration. Filter off all precipitate before titrating if the manganese is much above .60 per cent.

An excess of 5 per cent HCl gives low chromium results. Steels above 0.60 per cent manganese content give intensely red solutions, after addition of ammonium persulphate and, on boiling, yield chocolate-colored precipitates of oxides of manganese. When chromium is wanted the manganese oxide precipitates, if not destroyed, consume ferrous ammonium sulphate in the titration of chromium giving results for chromium that are too high.

It is safer to filter out this manganese oxide on account of danger of adding too much HCl when trying to redissolve it. No difficulty is experienced in titrating chromium and vanadium, *without* removing the tungsten by this persulphate method.

The above method is substantially the method as proposed by H. Walters, except the use of the internal indicator.

DETERMINATION OF CHROMIUM AND VANADIUM BY THE METHOD OF REMOVING THE BULK OF THE IRON WITH AMMONIA

For determination of small amounts of chromium and vanadium, dissolve 5 to 10 grams of steel in 50 c.c. 1 : 3 H_2SO_4, dilute with 50 c.c. of water, using a 600 c.c. beaker. After action is over, filter off the insoluble residue, wash it about fifteen times with dilute sulphuric acid. Call this filtrate and washings No. 1.

The insoluble residue is then washed off into the original beaker and held for further treatment, to be described later. It will contain much or little of the Cr and V, depending on the total percentage of carbides present. The filter paper may still contain a little V and C in its pores. Ash it in a porcelain crucible; dissolve it in a few drops of conc. HCl with heat; fume with 6 c.c. 1 : 1 H_2SO_4 to remove HCl. Add it to (A).

Dilute the filtrate No. 1 at once, to about 200 c.c., and add 1 : 1 ammonia slowly with constant stirring till a black precipitate forms. At this stage, add drop by drop about 2 c.c. of ammonia in excess to assure a complete precipitation of all the chromium and vanadium with very little iron.

Filter at once and redissolve in 50 c.c. 1 : 3 H_2SO_4. Wash paper twenty-five times with dilute sulphuric acid wash. Pour filtrate and washings into the original beaker containing the insoluble residue (volume at this point should not be more than 100 c.c.). Heat beaker for a while and add 40 s.c. of 1.20 HNO_3 to oxidize all carbides (A).

Continue to heat until any tungsten carbide present is yellow.

By this time vanadium and chromium will be in solution, or if no tungsten is present heat until all red fumes are gone and the residue is white and floating. Boil a few minutes and then add permanganate from a pipette a little at a time until a brown precipitate of manganese oxide forms that does not dissolve after twenty minutes' boiling. The boiling with permanganate brings the chromium and vanadium to their highest stage of oxidation.

Filter off the excess of manganese oxide together with some silicon and tungsten, if any is present. Use a heavy suction bottle and a porous crucible (zirconia crucible is preferred).

Wash the residue in the crucible about fifteen times with water only. Transfer filtrate to clean beaker, volume about 300 c.c. Finish as usual for chromium and vanadium with ferricyanide as an internal indicator. See pages 7, 8, 9, 10, 11, 12, and 18-25.

The advantage of the method of course is to remove the bulk of iron, thus enabling the operator to take larger weights of sample. In this way a steel containing 0.1 to 0.02 per cent Cr or V, or both, can be analyzed with just as much accuracy as one containing 1 or 2 per cent Cr, and 0.25 to 0.50 per cent V or higher.

TABLE SHOWING RESULTS OBTAINED BY METHOD ON KNOWN STEELS

Steel Taken, Grams.	Chromium Added, Per Cent	Results Found, Per Cent	Vanadium Added, Per Cent	Results Found, Per Cent	Blank c c
5	3.07	3.00	0.043	0.056	1.6
10 .	0.274	0.278	0.040	0.030	1.5
9	0.545	0.550	0.024	0.020	1.5
10	None	None	0.115	0.112	0.6
10	None	None	0.076	0.076	0.6
Cr, V, and W steel, 2 gms.	3.63	3.61	83	82	
Cr-V steel, 5 gms	1.06	1.08	254	244	
Cr-V steel, 8 gms	545	550	024	033	. . .
Cr-V steel, 5 gms	1.03	1.01	0.220	0.237	. . . .
U. S. No. 3) Std , 3 gms	1.37	1.37	0.215	0.22	.
Cr-V steel, 5 gms .	1.06	1.05	0.228	0.228	.
24 Cr-V steel, 5 gms	1.06	1.03	0.140	0.142	. .
Steel, 2 gms	None	None	1.913	1.879	0.3
Cr-V-W steel, 2 gms	2.75	2.72	3.19	3.23	. .

Carbon.—The high carbon, low silicon ferro-vanadiums decarbonize readily in the electric furnace with oxygen only. The lower carbon grades and high silicon varieties yield better if they are mixed with an equal weight of red lead, if burned in the electric furnace, or with four times their weight of red lead in the ten-burner Bunsen combustion furnace.

Nickel in Ferro-vanadium. Large amounts of vanadyl salts in solution yield ammoniacal citrates of a very dark green color. making it an impossibility to see end-points in a cyanide and silver titration. The *vanadic* salts are free from this objection: Dissolve 1 gram of the ferro-vanadium in a mixture of 30 c.c. of 1 : 3 sulphuric acid and the same quantity of 1.20 nitric acid. Use a little hydrofluoric acid and then evaporate to fumes with sulphuric acid, as already described in this chapter, if there should be an insoluble residue after heating with the mixed acids first mentioned. Boil the sulphuric and nitric solution, or the water solution of the fumed residue, with an excess of permanganate; filter out the oxide of manganese; wash it with sulphuric acid water. Neutralize the free acid in the filtrate with ammonia *before* adding the citric acid,* or the latter will reduce the vanadic to hypovanadic acid again. Then add a slight excess of ammonia to the clear solution and titrate the nickel in the regular way with cyanide and silver nitrate. (See Chapter IX.) If copper is present it will interfere, and the H_2S method given in page 9 is the simplest way to prevent the interference and to obtain the percentage of the latter element in the same analysis. Remove the copper before adding the citrate.

Manganese in Chromium and Vanadium Steels.—The manganese is obtained as in steels, by dissolving 0.050 to 0.100 gram of sample in 40 c.c. 1.20 nitric acid, boiling off red fumes, further boiling for four minutes with 1 gram of lead peroxide of a light brown color. Very dark brown to black-looking lead peroxide should be rejected, as the black-looking variety invariably gives low results. In the writer's experience with different lots, the black-brown peroxide gives results from 10 to 20 per cent too low. After boiling four minutes with the brown peroxide the solution is promptly put into cool water and from there into cold water. After the excess of lead peroxide has been allowed to settle for ten minutes, or more, if convenient, the pink solution is carefully decanted into a 5-ounce beaker and titrated with a standard solution of sodium arsenite until the pink shade is gone and the slight yellow of the nitrate of iron appears.

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* It is still better to add ammonium citrate made by neutralizing the citric acid with ammonia. This does away entirely with the vanadium green.

Chromium gives high results by the process just described and must first be removed as follows: Dissolve 0.150 or 0.30 gram of the chrome or chrome-vanadium steel in 5 c.c. of 1 : 3 sulphuric acid in a 250 by 25 mm. test tube, warming gently till action is over. Warm further with 10 c.c. of 1.20 nitric acid and boil off red fumes. Cool to room temperature; dilute to about 30 c.c. with water. Add a rather thick cream of zinc oxide until the ferric and chromic hydrates begin to settle, leaving a ring of clear fluid on the top. Continue the addition of zinc oxide *cautiously* until a slight excess is present, as shown by a *thin* layer of it settling to the bottom of the test tube. Avoid a *large excess of zinc oxide*, as it will cause an error in the volumetric measurements. Cool again and dilute to the 75 c.c. mark. Close the tube with a clean rubber stopper and mix the contents of the test thoroughly by repeated inversions of the tube. After the precipitate has settled somewhat, filter through a dry filter into a dry beaker. Rinse a 25 c.c. pipette three times with some of the filtrate and then deliver 25 c.c. into a 250 by 25 mm. test tube, add 15 c.c. of concentrated nitric acid, bring to boil, add lead peroxide, boil four minutes and finish as in plain steels. This process can be carried through in forty-five minutes and is entirely accurate for technical analysis to 2 per cent of manganese.

Manganese in High Silicon Ferro-vanadium that is Partially Insoluble in Acids.—Some ferro-vanadiums have been encountered that are partially insoluble due to high silicon, and perhaps also to high aluminum content. These types are rather rare. To obtain the manganese proceed exactly as described for the determination of manganese in the complete analysis of *ferro-aluminum-titanium alloy*, pages 47-48. If manganese only is wanted, 0.200 gram can be taken and fused in an iron crucible with a mixture of 2 grams of Na_2CO_3 and 1 gram of Na_2O_2 and then proceed exactly as described on pages 47-48 for the alloy of silicon-aluminum-titanium. Run blanks, as iron crucibles sometimes contain considerable manganese.

Sulphur.—Ferro-vanadium does not dissolve completely in dilute hydrochloric acid so that even approximate sulphur tests by evolution are not available. To determine sulphur in low silicon ferro-vanadium dissolve 3 grams of sample in 100 c.c. of concentrated nitric acid in a 600 c.c. beaker. When action ceases add immediately 50 c.c. of concentrated hydrochloric acid for, in alloys containing 35 and higher percentages of vanadium, a red precipitate settles out in large quantities if hydrochloric acid is not present to dissolve it. The presence of the red precipitate has a disadvantage. It causes the contents of the different beakers to spurt. Two grams of carbonate of soda are added. The solutions are transferred to No. 6 porcelain dishes and evaporated to dryness. The residue is dissolved in 100 c.c. of hydrochloric acid and evaporated again to dryness. Solution is once more effected with 50 c.c. of conc. hydrochloric acid followed by evaporation to a scum. Ten c.c. of concentrated hydrochloric acid are employed to dissolve the scum; 100 c.c. of water are added; the solution is filtered; diluted to 300 c.c. and the sulphate precipitated with barium chloride, using 60 c.c. of a saturated solution diluted with 240 c.c. of water. Blank determinations are made of exactly the same reagents and the sulphur found is deducted.*

One gram of highly silicious ferro-vanadium is fused with a mixture of 20 grams of sodium carbonate and 4 grams of potassium nitrate. The fusion is dissolved in water, acidulated with hydrochloric acid, evaporated twice to dryness, taken up with 20 c.c. of concentrated hydrochloric acid and sufficient water to dissolve the sodium chloride, and filtered. The sulphate in the filtrate is precipitated with barium chloride solution.

DETERMINATION OF ALUMINUM IN SOLUBLE FERRO-VANADIUM

Dissolve 1 gram of sample as far as possible with 1.20 nitric acid in a No. 5 porcelain dish. When all action is over, evaporate to dryness on a graphite bath. Ignite until all red fumes are gone over a Bunsen burner, or preferably in an electrically heated muffle furnace at a low red heat. Cool, then dissolve in about 20 c.c. concentrated HCl; heat until all chlorine fumes are gone, and all but the silica is in solution. Filter off silica, wash it free of iron test with 1 : 40 HCl. Smoke off filter paper in a platinum crucible; then increase the heat until the ash is free of charcoal. Add to the ash about 10 c.c. HF, and then 5 c.c. of 1 : 1 H_2SO_4, and when action is over, evaporate to thick fumes of SO_3. Cool; add water cautiously and heat until all is in clear solution. Transfer this solution to the main filtrate from the silica. Dilute all in an 800 c.c. beaker to about 300 c.c. Add cautiously from a small porcelain spoon, sodium peroxide until sufficient of it has been used to precipitate all of the iron; and the supernatant fluid is alkaline. (Keep the cover on the beaker as much as possible.) Then add 5 grams of Na_2O_2 in excess, and also 5 grams of Na_2CO_3. Bring just to a boil; cool; add paper pulp made from ashless filter paper. Stir the pulp well through the precipitate of hydroxide iron, etc. Use a ball of pulp about $\frac{3}{4}$ inch in diameter, filter the mixture of pulp and iron hydroxide through a double 12 centimeter paper. A small square of cheesecloth can be folded in with the filter paper at its apex to prevent the alkaline solution from tearing the paper.

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* Or fuse 1 gram with 8 grams of Na_2O_2 in an iron crucible; dissolve in water; acidulate with HCl, etc.

Wash the mixture of pulp and hydroxide of iron with sodium carbonate wash (5 grams dissolved in 500 c.c. water) about twenty times; stir the paper pulp during washing, bringing the bottom part of the mass to the top. Each washing to be effective must be thoroughly drained off before the next one is applied. This filtrate and washings contain the bulk of V and Al. Add to it slowly from a burette 1 : 1 HCl with constant stirring until the solution no longer turns turmeric paper even a faint brown but still reacts alkaline to litmus paper. $Al(ONa)_3+3HCl=3NaCl+Al(OH)_3$.

If considerable aluminum hydroxide separates out at this point, then the iron and pulp residue from the first peroxidation must be dissolved off in hot 1 : 1 HCl and thoroughly washed with 1 : 40 HCl. This filtrate and washings are peroxidized as before, using 5 grams peroxide and 5 grams of carbonate in excess, brought to a boil, cooled, filtered, and washed with carbonate water. The alkaline filtrate and washings are made neutral to turmeric paper and still slightly alkaline to litmus paper.

If very little aluminum separates out at this stage, that is, only a slight cloudiness occurs, then the third peroxidation of iron is not necessary. The aluminum hydroxide from the first and second peroxidations are filtered through the same double 9 or 12 centimeter filter, size of paper depending on the amount of precipitate.

Wash this mixture of aluminum hydroxide and paper pulp with ammonium nitrate wash (5 grams ammonium nitrate, 1 gram in 50 c c. of water) about thirty or forty times, upsetting pulp each time). Dissolve this precipitate of aluminum away from the pulp with hot 1 : 1 HCl, using about 30 c.c. of the acid. Pour the hot acid back and forth over the pulp, stirring same up well each time with a thin glass rod, then wash it about twenty-five times with 1 : 30 HCl, and then free of chlorine test to silver nitrate with water alone.

Save this filter paper and pulp to burn with the $Al_2O_3+V_2O_5$ obtained in the manner to be described, as it may still contain a little aluminum undissolved. This solution and washings from the pulp will contain the aluminum, and also a little vanadium and phosphorus. Heat this solution and washings to nearly boiling, adding a slight excess of ammonia and boil until ammonia smell is very faint. Ten or twenty minutes' boiling is sufficient, if but a slight excess of ammonia was added in the first place.

The aluminum hydroxide precipitate should now be free of occluded salts; mix it with paper pulp; filter; wash with ammonia nitrate water as before. Place the washed filter containing the $Al(OH)_3$ and pulp, after same has been well drained in a platinum crucible; smoke off the paper; add to it the filter paper and pulp from which the crude aluminum hydroxide was previously dissolved and which as stated may contain a little aluminum. When the smoke is all gone, raise the heat sufficiently to obtain a yellowish white residue. $Al_2O_3+P_2O_5+$a little V_2O_5+a little silica, the latter coming from the vessels used and from the filter ash. This residue is blasted mildly to constant weight, evaporated with about 6 c.c. of HF plus 5 or 6 drops 1 : 1 of sulphuric acid; evaporate to thick fumes. Drive off excess of SO_3; ignite to bright red and weigh. This weight gives the Al_2O_3+a little $V_2O_5+P_2O_5$. To correct for the V_2O_5 fuse the residue of oxides with twenty times its weight of sodium carbonate in a platinum crucible. Dissolve the fusion out in water; clean the crucible by heating in it a little dilute sulphuric acid. Add cleanings to the water extraction of the fusion which has meanwhile been made acid with H_2SO_4. Reduce the volume to about 150 c.c., then dilute the volume to exactly 200 c.c.; mix well, measure out 100 c.c.; boil this 100 c.c. with an excess of $KMnO_4$ and determine the vanadium in the solution as in steel. Calculate to V_2O_5.

The other 100 c.c. of $Al_2O_3+P_2O_5+V_2O_5$ solution is precipitated with a slight excess of ammonia; filtered; washed about twenty times with ammonium nitrate wash; dissolved off with hot HCl; washed with 1 : 40 HCl; this filtrate and washings are evaporated low; then converted to nitric by evaporating to 10 c.c. after adding 75 c.c. of conc. HNO_3; then finished for phosphorus, as in high vanadium steel, using the ammoniacal water solution of ammonium molybdate. Calculate the milligrams found to P_2O_5 by multiplying by the factor 2.2886, deduct twice the milligram of V_2O_5 found as described plus twice the milligram of P_2O_5 found from the total $Al_2O_3+P_2O_5$ and V_2O_5 and calculate the remainder to percentage of Al by use of the factor 53.033 and dividing by weight taken.

IRON DETERMINATION USING THE HYDROXIDE FROM WHICH THE ALUMINUM AND VANADIUM HAVE BEEN EXTRACTED BY PEROXIDATION

Get the sample in solution and remove all of the vanadium in the same manner as described for Al in the determination of the Al in soluble ferro-vanadium, pages 34–35. The V passing out with the Al. It may take as many as three peroxidations to remove all of the V. The vanadium-free hydroxide of iron is then converted into sulphate, and passed through the reductor and titrated with standard $KMnO_4$ as in iron ore. See pages 365–366.

THE DETERMINATION OF Al, Fe, Mn, Si, AND V IN PARTIALLY SOLUBLE FERRO-VANADIUM

Very high silicon and aluminum ferro-vanadiums are only partially soluble in nitric-hydrochloric mixtures. HF must be used except when S, Si, and P are wanted; for these three elements a fusion is necessary.

Silicon, Manganese, Sulphur, and Vanadium.—Fuse 1 gram of the finely ground alloy in a mixture of 10 grams of Na_2CO_3

plus 5 grams of Na_2O_2 in an iron crucible in the same way as described for ferro-titanium (see pages 47–48), getting the silicon, sulphur, and manganese exactly as described for the Si-Al-Ti-Fe alloy. Also aliquot parts of the total liter filtrate and washings from the silicon can be used for V by converting aliquot parts to nitrates or sulphates; then boiling with a slight excess of permanganate and finishing the V from this point on as in soluble ferro-vanadium. Run blanks including all chemicals and all operations, deducting the same.

Iron, Aluminum, and Manganese.—Dissolve 1 gram of the finely ground alloy in HF plus H_2SO_4 plus HNO_3 exactly as given for the Fe-Ti-Al-Si alloy (page 49), fuming to sulphates. Use aliquot parts of the liter solution for Al and Fe by peroxidizing the same in the manner as described for the vanadium alloy (see pages 35–37). Correct the Al for V_2O_5, P_2O_5, and SiO_2 in the manner given on page 37 for Al in soluble ferro-vanadium. Run blanks and known mixtures covering all operations.

Phosphorus.—Proceed by fusion as described on page 53 for Ti-Al-Si-Fe alloy up to the point where the solution of the hydroxides is evaporated to 15 c.c. with 100 c.c. of conc. HNO_3. Filter out the vanadic acid that separates out here; wash it with conc. nitric acid and finish the analysis in the manner given for ferro-vanadium on pages 41–45.

Nickel and Copper in the High Silicon Ferro-vanadium.—Dissolve the alloy by the HF plus H_2SO_4 plus HNO_3 method (see pages 74–75), converting all to sulphates as described and finish by removing the Cu by H_2S; evaporate the filtrate and washings to 100 c.c.; add a few crystals of potassium chlorate; evaporate to fumes; take up in water, heating to dissolve all the sulphates; and finish for Ni by the cyanide method as in steel. Also the ferricyanide method given on pages 205–212 can be used to advantage when very small per cents of the elements are present.

THE DETERMINATION OF IRON AND VANADIUM IN THE SAME OPERATION BY REDUCTION WITH H_2S

The writer has used the plan of dissolving the ferro in sulphuric and nitric acids, with a little hydrofluoric acid if necessary.

Evaporation to fumes and solution in water are the next steps. The vanadium and iron are then reduced with hydrogen sulphide, the solution is filtered,* hydrogen sulphide is removed with CO_2, and permanganate of potash standard is added until a pink is obtained or an old rose shade, that does not fade perceptibly after one minute's stirring. 2.5 c.c. of ferricyanide indicator are now dropped in, and a ferrous ammonium sulphate standard, 1 c.c. of which equals 1 c.c. of the permanganate, is added until three drops of this standard cause the light blue of the vanadyl solution to darken with the blue of the ferricyanide of iron. The number of c.c. of permanganate used to produce the old rose shade less the number of c.c. of sulphate required equals the number of c.c. of permanganate used to oxidize the iron, which number multiplied by 0.00556 gives the amount of iron in parts of a gram. The number of c.c. of sulphate used to produce a darkened blue, multiplied by 0.00508 (provided the sulphate exactly equals the permanganate), equals the number of grams or parts of a gram of vanadium present. (3.16 grams $KMnO_4$ *in one liter.*)

The iron residue from carbonate and niter fusions may be proceeded with for the estimation of the latter metal in this way: After removing the platinum, copper, etc., from the hydrochloric acid solution of the iron oxide by hydrogen sulphide, evaporate the filtrate and washings from the sulphides with a small excess of potassium chlorate. Remove the hydrochloric acid by evaporation to thick fumes with 60 c.c. of 1 : 1 sulphuric acid. Add water; dissolve by heating; reduce with metallic zinc; and titrate with standard permanganate for iron.

Copper.—If copper is present to any appreciable extent, as shown by the clouding with the ferricyanide indicator, it can readily be separated by hydrogen sulphide, passing the latter gas through the sulphate solution obtained by dissolving the sample in nitro-sulphuric acid, using a little hydrofluoric acid if much silicon be present, evaporating to fumes of sulphuric acid and dissolving in boiling water to hasten solution. (Copper can also be easily and quickly separated from this sulphate solution by neutralizing most of the free acid and precipitating the copper with an excess of potassium thiocyanate and sulphurous acid.) (Also see the author's ferricyanide separation.) The sulphide of copper is filtered, washed with hydrogen sulphide water, roasted free of paper in a porcelain crucible, dissolved in 1.20 nitric acid, and filtered from any insoluble sulphides or alumina. The filtrate and washings are made slightly alkaline with sodium carbonate water; 1 c.c. of ammonia is added and the solution titrated to disappearance of a blue with potassium cyanide standardized against 99.8 per cent metallic copper in the same manner.

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* Immediately after filtering out the sulphides, pass H_2S, again, for thirty minutes to reduce any iron that may have become oxidized during the filtration and washing of any metallic sulphides that may have formed. Then pass CO_2 to remove the excess of H_2S as above.

Molybdenum.—Molybdenum is separated exactly as the copper with hydrogen sulphide in slightly acid solution. The brown sulphide is roasted at a low heat in a porcelain crucible to a white or a bluish white residue (unless dark-colored oxides are present); then finish the determination exactly as described for molybdenum in steel (see page 156) by weighing the white to bluish white residue as crude MoO_3. Dissolve this MoO_3 in ammonia by warming it. Filter out the insoluble; wash it with ammonia water that has been filtered free of any impurities. Ignite the ammonia insoluble; weigh it; deduct its weight from the crude MoO_3. If the ammonia solution is blue, then copper is present. The ammonia solution must be nearly neutralized with nitric acid until it smells *faintly* but distinctly of ammonia. This blue solution can then be titrated with a standard KCN solution *slowly*, and with constant stirring, to the disappearance of the blue, as in steel. The copper so found is calculated to CuO and deducted from the weight of the crude MoO_3 after first deducting the weight of the ammonia insoluble. The weight remaining after these two deductions equals the pure MoO_3, which is reduced to metal by the use of the factor 0.6666.

The molybdenum sulphide must be burned off at the lowest possible heat, just below redness until the volatile matter is gone. Then the heat is raised cautiously to faintest possible red and maintained at this heat until the residue of crude MoO_3 is free of carbon from the filter paper. This is a most satisfactory method for weighing molybdenum for all percentages. The writer has used it for years.

Evaporation to fumes and solution in water are the next steps. The vanadium and iron are then reduced with hydrogen sulphide, the solution is filtered,* hydrogen sulphide is removed with CO_2, and permanganate of potash standard is added until a pink is obtained or an old rose shade, that does not fade perceptibly after one minute's stirring. 2.5 c.c. of ferricyanide indicator are now dropped in, and a ferrous ammonium sulphate standard, 1 c.c. of which equals 1 c.c. of the permanganate, is added until three drops of this standard cause the light blue of the vanadyl solution to darken with the blue of the ferricyanide of iron. The number of c.c. of permanganate used to produce the old rose shade less the number of c.c. of sulphate required equals the number of c.c. of permanganate used to oxidize the iron, which number multiplied by 0.00556 gives the amount of iron in parts of a gram. The number of c.c. of sulphate used to produce a darkened blue, multiplied by 0.00508 (provided the sulphate exactly equals the permanganate), equals the number of grams or parts of a gram of vanadium present. (3.16 grams $KMnO_4$ *in one liter.*)

The iron residue from carbonate and niter fusions may be proceeded with for the estimation of the latter metal in this way: After removing the platinum, copper, etc., from the hydrochloric acid solution of the iron oxide by hydrogen sulphide, evaporate the filtrate and washings from the sulphides with a small excess of potassium chlorate. Remove the hydrochloric acid by evaporation to thick fumes with 60 c.c. of 1 : 1 sulphuric acid. Add water; dissolve by heating; reduce with metallic zinc; and titrate with standard permanganate for iron.

Copper.—If copper is present to any appreciable extent, as shown by the clouding with the ferricyanide indicator, it can readily be separated by hydrogen sulphide, passing the latter gas through the sulphate solution obtained by dissolving the sample in nitro-sulphuric acid, using a little hydrofluoric acid if much silicon be present, evaporating to fumes of sulphuric acid and dissolving in boiling water to hasten solution. (Copper can also be easily and quickly separated from this sulphate

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* Immediately after filtering out the sulphides, pass H_2S, again, for thirty minutes to reduce any iron that may have become oxidized during the filtration and washing of any metallic sulphides that may have formed. Then pass CO_2 to remove the excess of H_2S as above.

Place filter containing washed precipitate in 150 c.c. beaker; add enough standard NaOH solution to cause the yellow color of the precipitate to disappear on macerating the paper to a pulp with a rubber-tipped stirring-rod. Dilute to about 30 c.c. with distilled water; add a drop of phenolphthalein solution, which should cause a deep red coloration, otherwise more standard NaOH solution is needed; then titrate back carefully with standard HNO_3 solution until the pink just disappears. Subtract total c.c. of acid used from total c.c. of alkali used. The difference in c.c. × 0.01 = precentage P.

TABLE I.—SHOWING EFFECT OF INCREASING AMOUNTS OF NITRIC ACID (1.42 Sp. Gr.) ON PHOSPHORUS RECOVERY *

Vanadium Added, Per Cent	15 c.c. HNO_3 Added, P Found	30 c.c. HNO_3 Added, P Found	40 c.c. HNO_3 Added, P Found	50 c.c. HNO_3 Added, P Found
None	0.121	0.121 0.122	0.121 0.120	0.121
0.20	0.119	0.121	0.121	
0.40	0.114	0.118	0.121	. . .
0.60	0.111	0.117	0.120	
0.80	0.110	0.116	0.121	
1.00	0.110	0.115	0.120	0.119
1.40	0.110	0.112	0.121	0.122
1.80	0.105	0.112	0.119	0.121
2.20	0.099	0.111	0.119	0.120
2.60	0.093	0.108	0.117	0.117

* This work was done with 1.63 g. samples of U. S. Bureau of Standards, 0.120 P standard, 10*b*.

Remarks.—The tests with the higher vanadium content were more tardy in precipitating than the lower ones, though all settled well after forty minutes' standing. Those to which 15 c.c. conc. HNO_3 were added gave deep-orange precipitates, darkening in color about in proportion to the vanadium content, clinging tightly to the stirring rods and beakers. The three highest vanadiums are lower in yield of phosphorus than the preceding ones because of the impossibility of detaching the adhering precipitate from the stirring rods.

Those with 30 c.c. conc. HNO_3 were an improvement in speed of precipitation, color of precipitate, and cleaning from beakers and rods. Those with 40 c.c. and 50 c.c. showed the best colored precipitates, i.e., nearest the normal yellow phosphomolybdate color and gave water-white washings, from which no recoveries of phosphorus were made. The 50 c.c. ones were a little prompter than the 40 c.c. though both sets were a vast improvement over the 15 c.c. and 30 c.c., and both cleaned very easily from beakers and rods and gave good results.

The precipitate from the 15 c.c. conc. HNO_3 in particular seemed to be finely divided and passed through the pores of the filter, necessitating reprecipitation of the washings in all those of higher vanadium content.

The vanadium was added as nitrate from an acid solution made as follows: Fuse 4.5 grams V_2O_5 (56.14 per cent V) with 10 grams Na_2CO_3 in a platinum crucible for ten to fifteen minutes. Let cool; place in a 400 c.c. beaker; add 10 c.c. water; then HNO_3 (1.20 sp. gr.) until effervescence ceases and 25 c.c. in excess. Rinse off crucible thoroughly with distilled water; cool solution to room temperature; transfer to 500 c.c. flask; dilute to the mark with water; stopper, and shake to mix thoroughly. 1 c.c. = 0.00505 grams V. 1 per cent V in 1.63 grams sample = 3.25 c.c. solution.

The vanadium was added after the tests were weighed and before the 45 c.c. HNO_3 (1.13 sp. gr.) were added. The vanadium was, in each instance, reduced from yellow to green, due to the action of the reducing gases liberated by the reaction between the acid and the steel. The 40 to 50 c.c. conc. nitric added just before removing from the fire caused the yellow vanadic color to return.

Solutions Required.—*Nitric Acid for Titrating.*—Dilute 35.4 c.c. HNO_3 (1.42 sp. gr.) to 4000 c.c. with distilled water.

Stock Solution of Sodium Hydroxide.—Dissolve 150 grams NaOH (c. p. sticks) and 1 gram $Ba(OH)_2$ in 1000 c.c. water. Stir well and allow to stand twenty-four hours. Filter off the clear solution (or decant if preferable) and dilute with an equal volume of distilled water. Put into a 2-liter bottle and close with a rubber stopper.

Sodium Hydroxide Solution for Titrating.—Dilute 566 c.c. stock solution to 8000 c.c. with distilled water.

Ferrous Sulphate Solution.—Dissolve 55 grams steel (low in phosphorus and sulphur) in 1000 c.c. beaker in 700 c.c. H_2SO_4

(1 : 3). Add a little water occasionally to prevent salting out, and heat gently, but do not boil. Filter, cool, and dilute to 1000 c.c.

Concentrated Potassium Permanganate Solution.—Dissolve 50 grams $KMnO_4$ in 1000 c.c. water.

Nitrate Wash.—Dissolve 8 grams KNO_3 in 8000 c.c. water.

Acid Wash.—Dilute 102.4 c.c. HNO_3 (1.42 sp. gr.) to 8000 c.c. with water.

Faintly Ammoniacal Water Solution of Ammonium Molybdate.—Into each of four 800 c.c. casseroles weigh 55 grams ammonium molybdate and 50 grams ammonium nitrate, and add 40 c.c. ammonium hydroxide (0.95 sp. gr.). Dilute each to 700 c.c. with water. Heat for about thirty minutes, stirring once in a while until all salts are in solution. Combine contents of the four beakers by pouring into a large bottle; then dilute to 4000 c.c. with water. Let stand overnight. Filter the insoluble material through double 15 cm. papers. *Do not wash.* The clear solution thus obtained should remain clear indefinitely. Do not filter out the insoluble material until the total mixture from the four casseroles has stood overnight diluted to 4000 c.c.

II. Method for Phosphorus in U. S. Standard Steels and Pig Irons to Which Have Been Added 28 Per Cent Vanadium and in Ferro-vanadium Containing 56.7 Per Cent Vanadium.—*Procedure.*—Weigh out 0.5 gram steel and 0.5 gram V_2O_5 (56.14 per cent V). Transfer to 250 c.c. porcelain dish. Digest with a mixture of 30 c.c. HCl (1.20 sp. gr.) and 30 c.c. HNO_3 (1.42 sp. gr.) for about one hour; then rinse off cover, add 100 c.c. HNO_3 (1.42 sp. gr.), and take to dryness. Bake five minutes at 750° C. in an electric muffle furnace.

Dissolve the oxides in 35 c.c. conc. HCl, evaporate to 10 c.c.; add 50 c.c. HNO_3 (1.42 sp. gr.), take to 10 c.c. volume, then add 10 c.c. more strong nitric and heat a while with cover glass on. Filter through a platinum or porcelain Gooch crucible with a thin pad of acid-washed asbestos, using suction. Wash fifteen times, using the following wash: 200 c.c. HNO_3 (1.42 sp. gr.), 100 c.c. water, and 20 grams $Fe(NO_3)_3$. (Ferric nitrate made by dissolving 5 grams low phosphorus, melting bar steel in 50 c.c. HCl (1 : 1) and taking to syrupiness twice with 50 c.c. HNO_3 (1.42 sp. gr.) each time.)

Concentrate the filtrate from the separated V_2O_5 to 10 c.c.

in 150 c.c. beaker and filter out the second crop of vanadium "rust" as before. A third concentration to 10 c.c. should show no "rust" (V_2O_5).

To the third concentration add 40 c.c. HNO_3 (1.42 sp. gr.), and bring to a boil; rinse cover and sides with water and precipitate with 50 c.c. of the faintly ammoniacal ammonium molybdate solution. Stir vigorously for about two minutes. Let stand one hour; filter and wash as described for steels containing up to 2.6 per cent V. Titrate with alkali and acid in the usual manner.

TABLE II—RESULTS OBTAINED USING THIS METHOD ON U S STANDARDS

No	Standard	V_2O_5 Added, Mg	P Found, Per Cent	Per Cent P Given by U S Govt
1	Iron D, *6a* V_2O_5	500	0 522	0 526
2	Iron D, *6b* V_2O_5	500	0 531	0 531
3	*10b* V_2O_5	500	0 124	0 120
4	*10b* V_2O_5	600	0 115	0 120
5	No. 20 Std V_2O_5	500	0 033	0 031
6	No. 20 Std. V_2O_5	600	0 033	0 031

In the above procedure an average of 0.007 per cent P was found in the V_2O_5 added.

TABLE III—PHOSPHORUS IN FERRO-VANADIUM, 56 7 PER CENT VANADIUM

Author's Method by Removal of about ⅔ of V_2O_5 and Pptn with faintly Ammoniacal Ammonium Molybdate Solution	V_2O_5 reduced with $FeSO_4$ and H_2SO_3 Pptn with Acid Molybdate Solution No V removed	Acid Molybdate Pptn No extra HNO_3 added No V removed	Faintly Ammoniacal Ammonium Molybdate Pptn plus 40 c c HNO_3 (1 42 sp. gr) No V removed.
Per Cent P	Per Cent P	Per Cent P	Per Cent P
0 414	0 240	0 053	0.185
0 418	0 232	0 108	0 183
0 397	0 235	.	.....
0 401	0 228		.....
. . .	0 234	.	.....
. .	0 260	. .	.....
. . .	0 220	. . .	.....

Silicon.—For silicon dissolve 1 gram of the finely ground ferro in 50 c.c. 1.20 nitric acid. Add 30 c.c. 1 : 3 sulphuric acid and evaporate to fumes. Dissolve the sulphates in water, heating until all but silicic acid is in solution. Filter. Wash with dilute hydrochloric, then with water. Ignite and weigh as usual. If the sample contains much silicon and does not yield to the nitric acid, filter out the insoluble residue; wash it first with hydrochloric acid and then with water; roast off the paper in a platinum crucible. Fuse the residue with twenty times its weight of sodium carbonate plus $\frac{1}{5}$ its weight of potassium nitrate. Dissolve the melt with water. Acidulate it with hydrochloric acid and add the clear solution to the portion dissolved by the nitric acid, and evaporate all to fumes with 30 c.c. of 1 : 3 sulphuric acid, and finish as in low silicon ferro-vanadium.

CHAPTER III

THE ANALYSIS OF FERRO-ALUMINUM - SILICON - TITANIUM, OF NEARLY SOLUBLE FERRO-TITANIUM, AND TITANIUM STEEL

Ferro-Aluminum-Silicon-Titanium.—Fuse 1 gram of the finely ground metal with a mixture of 10 grams of Na_2O_2 plus 5 grams of Na_2CO_3 in a covered iron crucible. Apply low heat until the substance is thoroughly liquid. Keep molten about two or three minutes at a dull red heat. The best dimensions for the iron crucible are 2½ inches top diameter by 1¼ inches bottom diameter by 1½ inches high. Dissolve the fusion out in water; washing same into a dish or casserole. Acidulate the fusion with HCl; heat until all action is over, with the cover on the casserole. Remove cover; rinse under side of same off into dish; evaporate to dryness. Dissolve the dry residue in dish by warming it with about 30 c.c. 1 : 1 HCl; then heat further after adding about 75 c.c. of distilled water; cool; add paper pulp about ½ inch to ¾ inch ball; stir pulp in well; filter; wash free of iron test with 1 : 40 HCl, then with water until free of chlorine test to silver nitrate.

Smoke off the filter paper, etc., until ash is white in a 20 c.c. to 25 c.c. platinum crucible. Apply the heat cautiously, finally raise it to low red; then blast slowly to constant weight, cool; add, a little at a time, to the crucible, 15 c.c. HF; then 2 c.c. of conc. H_2SO_4; evaporate to thick fumes; heat to a dull red and weigh. The difference between this last weight and the weight after blasting to constant weight equals silica, which is calculated to percentage of silicon by use of the factor 46.93.

The residue in the crucible after HF evaporation may contain some aluminum and titanium. It should be fused with twenty times its weight of Na_2CO_3 at a bright red heat for twenty or thirty minutes; dissolved out in water; the crucible is cleaned by warming in it some 1 : 1 HCl; wash these cleanings of the crucible into a small beaker together with the water solution of the fusion; add to this about 20 c.c. of 1 : 1 HCl and heat till all is in solution.

Silicon.—Add this solution to the main filtrate from the silica; this main filtrate is now evaporated again to dryness, if it is desired to get the last traces of silica. This last silica should be treated exactly like the first main silica. The loss of weight obtained from the second small silica residue from this second evaporation plus the loss of weight obtained from the first main silica equals the total silica. This is calculated to silicon by use of the factor 46.93. The final filtrate and washings from the second evaporation made to get out the last traces of silica combined with cleanings from both evaporations with HF and H_2SO_4 will contain the total phosphorus, sulphur, titanium, aluminum, and manganese, also copper or nickel if any are present in the alloy.

Manganese.—Dilute the solution containing the total Al, Ti, P, and Mn to 1 liter. Mix well; rinse a 100 c.c. burette several times with 5 c.c. portions of this solution; then fill the burette with it and measure off with this burette a 100 c.c. and a 50 c.c. portion. It is very important that the liter flask be calibrated with the same burette. Make sure that the 100 c.c. burette delivered ten times with distilled water into the dry liter flask, fills it exactly to the mark at room temperature. If the burette does not agree with the liter mark, the flask should be marked at a point where it does agree with the burette. Evaporate the two aliquot parts to thick fumes with 20 c.c. of 1 : 3 sulphuric acid. Redissolve by heating with 10 c c. of water. Rinse out this solution into a manganese tube; add 15 c.c. of conc. nitric acid and dilute to 35 to 40 c.c. with water. Finish for manganese as in plain steel. If the manganese by this method is found to exceed the 3 per cent it will be better to run new 50 to 100 c.c. portions. Remove the iron with zinc oxide and finish in the manner described for 10 to 15 per cent manganese steels. See pages 345–346.

Sulphur.—Measure off with the same burette 500 c.c. of the liter solution: precipitate the titanium, iron, and aluminum in hot solution with a slight excess of ammonium. Filter and wash the hydroxides of titanium, aluminum, and iron thoroughly with water. Filtrate and washings contain total sulphur from ½ gram of sample; add 10 c.c. excess of conc. HCl to 400 c.c.

volume and precipitate the sulphur with $BaCl_2$. Finish as in sulphur in steel. The precipitate of aluminum, titanium, and iron hydroxide can be used for titanium and aluminum by separating the titanium and iron from the aluminum by several peroxidations.

Titanium and Aluminum.—The iron and titanium after being freed from aluminum by several peroxidations can be dissolved in HCl and evaporated to fumes with H_2SO_4, taken up again in water and H_2SO_4 by heating; and made nearly neutral with ammonia. The titanium is then precipitated with sodium thiosulphate in the manner to be described later.

However, as these hydroxides contain much iron from the iron crucible in which the peroxide fusion was made, it is better to start with a 1-gram portion of the alloy in a covered platinum dish as follows: Add 10 c.c. HF conc. with cover on, warm in a good draught; remove from heat; add a few drops of conc. nitric; when action ceases, continue to add conc. nitric until a total of 5 c.c. of conc. nitric have been used. When action is over, remove lid; wash under surface of same off into dish; add 10 c.c. of conc. sulphuric acid; evaporate to thick fumes; take up in 30 c.c. 1 : 1 H_2SO_4; heat until all is in clear solution, adding a little water if necessary to dissolve the sulphate of iron. Black or insoluble residue such as graphite does not need to be recovered.

Transfer to an 800 c.c. beaker, dilute to 350 c.c., add Na_2O_2 until solution is alkaline, keeping covered as much as possible. Then add 5 grams of sodium peroxide and 5 grams of Na_2Co_3 in excess. Bring just to a boil; cool; filter; wash with sodium carbonate wash (5 grams to 500 c.c. water); wash about forty times, upsetting paper pulp and precipitate with each washing.

The alkaline filtrate and washings are titrated with 1 : 1 HCl, until the solution is neutral to turmeric and still slightly alkaline to litmus paper. If much precipitate of aluminum separates out, the iron, titanium, etc., hydroxides on the filter must be redissolved in 30 c.c. hot 1 : 1 HCl, filtered; pulp washed (pulp and filter paper saved), reperoxidize the solution of the hydroxides as before. The alkaline filtrate and washings are neutralized as before; if only a slight cloud of $Al(OH)_3$ is obtained after several hours' standing, then no further peroxidations are necessary. The $Al(OH)_3$ precipitates from the various peroxidations and neutralizations are each washed about twenty-five times with ammonium nitrate (5 grams dissolved in 500 c.c. water). These hydroxides of aluminum are redissolved in hot 1 : 1 HCl; filter and pulp thoroughly washed with water. This pulp and filter paper are saved to burn with the main Al, which is now precipitated from the above Al solutions of the crude $Al(OH)_3$. This is done by adding a faint excess of ammonium to the Al solution. Boil a few minutes; cool; and filter, after adding paper pulp; wash free of chlorine in the manner described as before with ammonium nitrate.

Smoke off the mixture of pulp and $Al(OH)_3$ in a 25 c.c. to 30-c.c. crucible together with the filter papers and pulps from which the crude $Al(OH)_3$ was dissolved.

When the residue is white, blast it to constant weight as Al_2O_3 and a little SiO_2. No phosphorus should be present in this, as the alloy was dissolved in hydrofluoric acid. Remove the small amount of silicon by evaporating to thick fumes with 6 c.c. 1 : 3 sulphuric acid plus 6 c.c. of HF; drive off cautiously the excess of H_2SO_4; ignite to constant weight as pure Al_2O_3, which, multiplied by 53.033, gives percentage of Al when 1 gram is taken.

The iron and titanium hydroxides left on the filter after the last peroxidation to remove Al are dissolved off as far as possible with hot 1 : 1 HCl, filter paper and pulp are then washed thoroughly with water: hold this filtrate and washings as the main iron and titanium solution. The paper and pulp together with each of the filter papers and pulps from which the iron and titanium hydroxides were dissolved off before each previous peroxidation are smoked off together in a platinum crucible at a low red heat until all paper is removed. Weigh the ash. If it weighs more than a milligram, fuse it with twenty times its weight of Na_2CO_3 at a bright red heat for twenty to thirty minutes; dissolve out the melt in water by heating; filter; wash with Na_2CO_3 water. Acidulate the filtrate and washings with HCl; boil off most of the CO_2; make slightly alkaline with ammonia; heat; if any white hydroxide separates out, calculate it to Al and add it to the main aluminum already found. The residue which was filtered out of the water solution of the sodium carbonate fusion just mentioned, and then washed with sodium carbonate water, may contain some Fe and Ti.

To make sure of getting this Ti in solution, it is safest to burn the filter containing the small amount of Fe and Ti to an ash. Again fuse the ash with twenty times its weight of Na_2CO_3 for thirty minutes at a bright red heat. Dissolve the fusion out of the crucible with hot water and transfer it to a beaker; make the solution of the fusion just acid with HCl; evaporate it if necessary to 30 c.c.; add 20 c.c. conc. HCl; boil slowly for twenty minutes to make sure the titanium is all dissolved; filter out any insoluble matter. If any insoluble matter be found, it must be filtered out; washed; ignited and weighed; evaporated with 3 c.c. 1 : 3 H_2SO_4 and 6 c.c. HF; ignited and weighed again. Any loss of weight equals silica, from this silica deduct any similar silica found in the blank, calculate the remainder as part of the silicon found in the sample. If any appreciable residue remains in the crucible after the above procedure, its weight less any similar weight found in the blank must be calculated to Ti and added to the total Ti found in the sample.

The filtrate and washings from the last mentioned insoluble matter are added to the main iron and titanium solution. Now transfer this main solution to a 500 c.c. flask. If its volume is greater than 500 c.c., evaporate it to about 350 c.c. and then make the transfer; dilute to the mark and decant off exactly 250 c.c. into a porcelain dish or a casserole. Add to the casserole also 40 c.c. of 1 : 1 H_2SO_4 and evaporate to thick fumes. Redissolve by heating with 20 c.c. 1 : 1 sulphuric acid until all sulphate of iron and aluminum have been dissolved and there remains only a clear or slightly cloudy solution. Neutralize most of the free acid with ammonia. Add 5 grams of sodium thiosulphate for every 50 mg. of titanium supposed to be present; boil gently for one-half hour; filter off titanium, using some paper pulp. Wash with sulphurous acid water (2 c.c. conc. sulphurous acid water in 500 c.c. of water) until free of iron test. The washed precipitate and pulp are smoked off and ignited till white or slightly brownish white at a low red heat. To make sure of the absence of iron in this ash, it can be fused with 5 grams $KHSO_4$ as follows: Heat the crucible containing the TiO_2 plus 5 grams $KHSO_4$ very gradually at first, to prevent crawling and spattering, until all the water has gone from the flux with a white flame of a Bunsen burner, keeping below redness until white fumes of SO_3 begin to appear, then increase flame gradually until low redness is reached on the lower half of the crucible; continue to heat at a low temperature until all is in a state of clear transparent fusion; and SO_3 is coming off rather briskly; cool; run the melt on up the sides of the crucible.

Place the crucible in a 250 c.c. casserole with 50 c.c. water plus 50 c.c. 1 : 3 H_2SO_4; dissolve with heat; do not filter; heat until all sulphate is dissolved; and there remains only a little white floating insoluble matter. Transfer to a beaker; dilute to 300 c.c.; nearly neutralize with 1 : 3 ammonium, and while still acid add 5 grams of sodium thiosulphate for every 50 mg. of TiO_2 supposed to be present. Boil twenty to thirty minutes; filter; wash free of sulphate test to barium chloride; and then thirty times more. Smoke off filter paper and pulp until all char is gone; ignite at a red heat to constant weight; evaporate with 5 c.c. conc. HF plus 6 c.c. 1 : 3 H_2SO_4; be sure there is an excess of sulphuric acid, otherwise titanium fluoride will sublime and be lost. If the under side of the crucible lid is covered with a white coating, then some titanium has been lost as fluoride, due to insufficient H_2SO_4. However, avoid a great excess of sulphuric acid, as it is difficult to remove, and ignite finally to dull red and weigh as pure titanium oxide, free of all aluminum, silica, and iron; multiply this weight by 60.04 and divide by weight taken, that is, 0.50 gram, the original gram having been divided into equal portions of 250 c.c. All Zr is with the Ti.

The other 250 c.c. portion of the hydrochloric solution in the 500 c.c. flask is analyzed for iron by reducing this heated solution with a slight excess of stannous chloride, titrating with standard dichromate as in iron ore (see pages 442–443).

This iron solution cannot be converted to sulphate solution and passed through the zinc reductor for the reason that part of the titanium in solution would be reduced by the zinc and would be counted as iron. Titanium in solution does not interfere when the iron is determined by stannous chloride and potassium dichromate.

Blank for S, P, Mn, and Si.—Blanks for method used on insoluble ferro-titanium should be run by fusing a standard pig iron or finely divided steel drillings of known content together with enough pure titanic oxide to about imitate the sample. This blank will be best for the phosphorus, sulphur, silicon, and manganese, allowing of course for the Mn, P, S, and Si, in the standard pig iron. The U. S. Bureau of Standards gives the titanium content of the pig iron standard that it furnishes. Any excess of P, Ti, S, Si, or Mn, over or above that given for the standard pig iron is deducted as a blank correction for reagents from the results obtained on the sample being analyzed.

Aluminum and Iron Blank for Insoluble Ferro-titanium.—Place in a platinum dish 0.4 gram of U. S. Bureau of Standards Sibley ore together with about as much pure titanic oxide as there is titanium in the sample. Evaporate this mixture with HF and a little nitric acid and then fume with H_2SO_4; for Al dissolve weighed amounts of metallic Al powder in a little HCl and add the solution to the sulphuric acid solution of the Sibley ore just before peroxidizing to remove Al from the Ti and Fe, and finish in the same way as in the method described for the sample. Any iron or aluminum found in excess of that added to the standard is deducted from the iron and Al found in the sample.

Phosphorus.—Fuse 1 gram of sample in an iron crucible in the same manner as described for silica, sulphur, and titanium. Dissolve out fusion; acidulate with hydrochloric acid as described for sulphur and silica. Evaporate to dryness to remove bulk of silica; take up as described in HCl acid. Filter out silica, wash free of all iron, test with 1 : 1 HCl, ignite to weigh. This silica should be then evaporated with H_2SO_4 and HF; ignite the residue, after evaporation to remove excess of H_2SO_4. Fuse with twenty times its weight of sodium carbonate. The fusion is dissolved out in water; acidulated with HCl; heated to clear solution and added to the main filtrate from the silica. Precipitate the total solution with ammonia to remove sodium salts; wash the hydroxide precipitate about ten times with water; dissolve the precipitate with about 30 c.c. 1 : 1 HCl. Wash paper pulp until free of iron test, evaporate filtrate and washings in porcelain dish; then add 100 c.c. of conc. nitric acid, evaporate to 15 c.c.; filter out any titanic oxide that separates out and wash it twenty times with 1.20 sp. gr. nitric acid; volume should not be over 25 c.c.; evaporate to 20 c.c. if necessary in phosphorus beaker (125 c.c. beaker); add 20 c.c. conc. nitric acid; bring just to a boil; remove from flame; rinse down sides of beaker with fine jet of water. Volume should now be about 50 c.c. Add to the hot nearly boiling solution 50 c.c.

of the slightly ammoniacal water solution of ammonium molybdate, stir well and filter out the ammonium phosphorus molybdate as soon as settled, and finish the phosphorus as in steel. Calculate the percentage to a 1-gram basis.

The titanic acid that is filtered out may carry with it a little of the phosphorus. Ignite it at a low red heat in a platinum crucible until paper is gone. Fuse the ash with twenty times its weight of Na_2CO_3 at a bright red heat for thirty minutes; dissolve the fusion out in water; filter out the insoluble titanic acid; wash it with sodium carbonate water; acidulate the filtrate and washings with HCl; heat until CO_2 is nearly all removed; add enough ferric chloride solution to give a red precipitate with ammonia. Heat; filter off the red precipitate; wash it a few times with water. Dissolve the precipitate off with hot 1.13 sp. gr. nitric acid; wash free of iron with dilute nitric wash. Evaporate filtrate and washings to 10 c.c.; precipitate the phosphorus as in steel with ammonium molybdate solution, and add to the main phosphorus percentage.

Put finely divided standard pig iron through all of the above methods, and any phosphorus found above its true percentage is deducted from that obtained from the ferro-titanium, the remainder being the true phosphorus in the ferro-titanium.

Second Method for Manganese in Fe, Ti, Si, Al Alloy.—As the so-called iron crucibles sometimes contain considerable manganese there is some advantage in running the manganese by taking a separate portion and getting it into solution exactly as for the iron with HF and a little conc. nitric. Then evaporate

ANALYSIS OF TWO DIFFERENT MAKES OF IRON CRUCIBLES*
SHOWING HOW THE MANGANESE VARIES

	Older Make, Thicker Wall 025 inch Thick Crucible	New Make, Thinner Wall 018 inch Thick Crucible
C	03	.15
Mn.	Trace	60
P.	051	013
S	011	.035
Si	040	.009
Cu	.015	026

After pickling the outer surface in HNO_3 (1.20).

to fumes with H_2SO_4. In this way variations due to high blanks are avoided, or when the sample is dissolved in this manner for Al, Ti and Fe, the total sulphate solution can be diluted to 1000 c.c aliquot parts taken for Mn The balance of the solution can be measured off for Fe, Al, and Ti as already described.

The crucible showing high manganese and high copper is the most resistant to alkaline fusions. The new thin wall crucible shows a total of 0.285 per cent Cu when the surface of the crucible is not pickled thoroughly with HNO_3 (1.20). The copper shows plainly on the lower third of the outer wall of the crucible in a coating. The older make shows no copper on surface, and the 0.015 is its total copper.

Nearly Soluble Ferro-titanium.—The finely ground sample is gotten into solution as far as possible with H_2SO_4, the unsoluble residue is filtered out, washed, ashed and fused with 5 grams of sodium carbonate plus 20 mg. of potassium nitrate in a platinum crucible in a bright red heat until it is molten, then keep at a bright red heat for twenty to thirty minutes; fusion is dissolved out in water; the crucible is cleaned by warming in it a little 1 : 1 HCl; the solution and cleanings are added to the first main filtrate, this filtrate is then finished for silicon, iron, aluminum, titanium, and manganese by the same method that was used where the insoluble alloy was fused in an iron crucible with a mixture of sodium peroxide and sodium carbonate.

As the fusion is not made in the iron crucible, the solution can be used for iron also, but not for sulphur or phosphorus. The sulphur and phosphorus must be obtained by peroxide and sodium carbonate fusion of a separate portion as described for insoluble ferro-titanium.

Iron Blank.—Fuse at a bright red for thirty minutes enough U. S. Bureau of Standard Sibley iron ore and titanic oxide (prepared as directed) with 5 grams Na_2CO_3 plus 20 milligrams KNO_3; fuse about as much TiO_2 and iron ore as the sample contains.

Dissolve fusion out in water, clean crucible with a little HCl; add the cleanings to the water solution of the fusion; add to this the same amount of H_2SO_4 as is used to dissolve the finely ground sample; add also as much Al dissolved in a little HCl as is likely to be in the sample. Peroxidize to remove Al as many times as the sample is peroxidized. The hydroxides left on the filter after the last peroxidations together with each of the filter papers and pulps from which the iron and titanium hydroxide were dissolved off before each peroxidation, are smoked off together in a platinum crucible at a low red heat until all paper is removed.

Cool the ash, which consists of titanium and iron, free of aluminum. Shake this out into a small beaker. Clean out the crucible with a little 1 : 1 HCl, using heat, wash this cleaning into the same beaker; remove any adhering particles. Add to the ash in the beaker 20 c.c. conc. HCl and heat until all is dissolved except a white floating residue, if any. If this white floating residue amounts to more than a milligram on being burned in a platinum crucible and weighed, then fuse it with twenty times its weight of Na_2CO_3 at a bright red heat for twenty to thirty minutes; dissolve out the melt; get in clear solution in a small beaker, by heating it with 1 : 1 HCl; then add the clear solution to the filtrate and washings from the white floating residue; now transfer this filtrate and washings to a 500 c.c. volumetric flask, dilute to the mark; mix well and decant off exactly 250 c.c. Analyze for iron by reducing this heated solution with a slight excess of stannous chloride, titrating with standard dichromate as in iron ores (see pages 442–443).

Sulphur by Evolution at 900° C. to 950° C.—Sulphur on soluble and insoluble ferro-titanium can be gotten by evolution in a stream of hydrogen, carrying HCl, at 900° C. to 950° C. in a tapered combustion tube. Weigh out 0.5 gram of the finely powdered alloy into a porcelain or clay combustion boat and proceed as described on pages 122–129.

Result by Fusion	Evolution in Hot Tube
.15 per cent S	.15 per cent S

PREPARATION OF 99.5 PER CENT TiO_2.

Grind black Norwegian rutile to the finest flour in an agate mortar. Fuse 1 gram of this powder with 20 grams $KHSO_4$ in the following way: heat very cautiously below redness until the absorbed water is all gone from the $KHSO_4$; then raise the heat very slowly until the crucible is a dull red on the bottom. Continue to heat at a low red until all is in a state of quiet fusion and so clear that one can see nothing but a few white particles of silica floating in the otherwise clear melt.

Run the fusion well up the sides of the crucible. Place crucible and all in about 50 c.c. of 1 : 3 H_2SO_4 in a porcelain dish and heat until all is dissolved except a few white floating flakes of silica. Cool; remove crucible; filter; and wash with dilute sulphuric (1 : 40) about fifty times.

The filtrate and washings are nearly neutralized with ammonia, but while still distinctly acid, dilute to 800 c.c. with water and boil. Titanium acid will separate out and settle to the bottom. Pour off the supernatant liquid and wash several times by decantation; then add a ball of ashless filter paper pulp; stir this well with the titanic acid; filter, and wash free of sulphate to $BaCl_2$ test. Ignite and weigh. Residue should be at least 99.5 per cent pure titanic oxide.

Method of Making Sodium Carbonate—Sodium Peroxide Fusions.—Sodium peroxide and sodium carbonate mixture fusions, in general, are made as follows: Mix the carbonate and peroxide together in a clean iron crucible, using a stout Ni-chrome wire for a stirrer.

Pour about half of this mixture into another iron crucible in which the fusion is to be made. Place on top of this the powdered, weighed sample. Mix all with the stirring rod and cover the mixture with the other half of the fusion mixture; then heat gently until all is in quiet fusion, which should take about one or two minutes. While in the molten condition, take the crucible in the tongs, keeping it in the flame all the while, and give it a slight swirling motion for two or three minutes more; and no longer. Cool; place the crucible on its side in a covered casserole or porcelain dish.

Add water and heat until the melt is dissolved. Remove the crucible; rinse its walls off thoroughly; rub out any adhering particles from its inner walls. Rinse all into the dish. The contents of the latter are then ready for the acidulation and evaporation to remove silica.

Nickel, Chromium, and Vanadium in Ferro-titanium.—Get the sample into complete solution by the method given for ferro-aluminum-titanium-silicon, proceeding exactly as described to the point where the silicon has been removed; evaporated with HF, etc., and the residue from the HF plus a few drops of H_2SO_4 has been fused; dissolved; and added to main filtrate from the silica. This solution will now contain all of the Ni, Cr, and V. It can be then converted to sulphates by taking it to *slight* fume of SO_3 by evaporating it with 50 c.c. of 1 : 3 H_2SO_4. Add 100 c.c. of water and 10 c.c. more of the sulphuric acid; heat until all sulphates are in solution; repeat the evaporation to insure the entire removal of the HCl. Be careful each time to take only to the slightest fume as chromium is very insoluble if fumed strongly.

Finish for V, Cr, and Ni as in steel.

Iron in Soluble Ferro-titanium—By Reduction with Hydrogen Sulphide.—Dissolve 0.5 gram of sample in 1 : 3 sulphuric acid. If there be any insoluble residue that is not white, filter the same out and wash it with dilute sulphuric acid. Roast it. Fuse it with potassium bisulphate. Dissolve the melt in dilute sulphuric acid and add it to the filtrate and washings from the insoluble residue. Dilute the slightly acid filtrate and washings to 200 c.c. Pass hydrogen sulphide through the same until the iron is entirely reduced. It will be colorless when hot. The reduction will take about an hour, with the gas passing at a rather rapid rate. Filter the solution into an 800 c.c. boiling flask. Wash the filter with 1 : 10 sulphuric acid until free of iron test. Pass hydrogen sulphide through this filtrate for one hour more. (Saturate the acid wash with H_2S before using.)

Now pass a stream of carbon dioxide through the solution, keeping it at boiling temperature during the time that the CO_2 is passing. When a piece of filter paper, moistened with a water solution of lead acetate, is no longer discolored, even slightly, when held in the neck of the flask, the excess of hydrogen sulphide is all driven out. Place the flask in cold water with the stream of carbon dioxide still passing through it. The glass tube that carries the H_2S and CO_2 into the fluid should, of course, reach nearly to the bottom of the boiling flask. When the contents of the flask are cold, titrate with standard permanganate of potash until one or two drops yield a pink color that is permanent for several minutes. The same standard that is used for titrating iron in ferro-vanadium can be utilized in this determination. One c.c. of the standard equals 0.00556 gram of metallic iron (3.16 gram $KMnO_4$ in one liter.)

The residue on this filter will contain all of the copper present which can be roasted and finished as in steels for Cu.

Manganese in Ferro-titanium Soluble in Sulphuric Acid.—Dissolve 0.100 gram in 10 c.c. 1 : 3 sulphuric acid. Add 10 c.c. concentrated nitric acid. Boil off red fumes. Dilute to 35 c.c. with water and finish as in steels. This applies to manganese not in excess of 1 per cent. Use 0.05 gram for manganese content exceeding 1 per cent. Accurate to 2 per cent Mn. For higher percentages of manganese dissolve 1 gram of sample in 30 c.c. 1 : 3 sulphuric acid.* Oxidize by boiling with 10 c.c. conc. nitric acid and 1 gram of potassium chlorate. Add 60 c.c. 1 : 3 sulphuric acid and evaporate to thick fumes. Cool, add water and heat until all is dissolved except perhaps some of the titanic oxide and silicic acid. Be sure that all iron and manganese sulphates are in solution. Wash the cold solution into a liter flask. Fill the flask one-half full with distilled water. Add a rather thick paste of manganese-free zinc oxide and distilled water. Continue the addition of the zinc oxide until the iron and titanium settle out well, avoiding any unnecessary excess of the zinc oxide. Cool, if necessary, to the temperature of the room, and dilute the contents to the liter mark with distilled water. Mix ten times, inverting the stoppered flask each time.

Permit the precipitate to settle for a half-hour with the flask in an inclined position. Pour the supernatant fluid through a large, dry filter into a dry beaker. Use two filters to hasten matters. Rinse a 100 c.c. pipette three times with portions of the filtrate. Then draw out a 300 c.c. portion and a 400 c.c. portion. Place these in separate boiling flasks, labeling them 300/1000 and 400/1000, respectively. Add 2 drops of 1.20 nitric acid to each of these aliquot parts. Heat the 300 c.c. to boiling, and titrate with standard permanganate of potassium, adding a little at a time. Shake thoroughly with each addition of the permanganate solution, reheating the solution between times. When 3 drops finally produce a slight but distinct pink color in the hot supernatant fluid, after a reheating and thorough shaking, the end-point is reached. Deduct 0.2 c.c. from the total permanganate used. Multiply its value per c.c. in milligrams of iron by 0.2951 to find its value in milligrams of manganese.

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* One can also finish from this stage on as directed on page 345 by the author's method for manganese above 2 per cent.

Titrate the 400 c.c. part in like manner and average the two results, calculating them as 3/10 and 4/10 of a gram respectively. (See also Mn in Insoluble Ferro-titanium.)

Standardization of the Permanganate Solution for Iron and Manganese.—Weigh 3.16 grams of c.p. potassium permanganate crystals into a liter flask. Dissolve in distilled water and dilute to liter mark.

Weigh 0.2850 gram of c.p. recrystallized oxalic acid into a 200 c.c. beaker. Dissolve the crystals in 100 c.c. of hot water. Add 30 c.c. 1 : 3 sulphuric acid and titrate this hot solution with the permanganate solution. This latter should not be standardized for, at least, twelve hours after it has been dissolved and made up to 1 liter.

This amount of oxalic acid will require usually 45.50 c.c. of permanganate of the above strength to render it a faint pink that is permanent for several minutes. As the oxalic value of a permanganate solution multiplied by 8/9 gives its iron value therefore the latter is found by this calculation: $0.2850 \div 45.50 \times 8/9 = 0.005567$, or 1 c.c. of the permanganate equals 0.005567 gram of metallic iron. This value multiplied by 0.2951 yields the value of the same solution in grams of manganese, or $0.005567 \times 0.2951 = 0.001642$ gram of manganese. For check 0.280 gram oxalic acid took 44.8 c.c. $KMnO_4$, or $0.280 \div 44.8 \times 8/9 = 0.005555$ and $0.005555 \times 0.2951 = 0.001639$, or 1 c.c. = 0.001636 gram of manganese. Average iron value equals 0.00556 gram and average manganese value equals 0.001640 gram per c.c. Compare the theoretical factor for manganese with that found by standardizing the permanganate standard by putting a ferro-manganese, containing a known per cent of manganese, through the identical process of precipitation with zinc oxide, etc.

Silicon in Soluble Ferro-titanium.—Dissolve 1 or 2 grams of drillings as in steels. Evaporate to fumes of sulphuric acid. Dissolve in water. Filter, wash, ignite, weigh, evaporate with

The following reaction show how Volhard's method proceeds:

$$3MnSO_4+2KMnO_4+2ZnO=K_2SO_4+5MnO_2+2ZnSO_4.$$

a few drops of conc. sulphuric acid, and the usual amount of hydrofluoric acid. Ignite and calculate the loss of weight as silicon. Should a white coating appear on the lid of the crucible when the sulphuric acid is being driven off, it means that there has not been a sufficient amount of sulphuric acid added, some of the titanium having volatilized as fluoride.

In such event, repeat the analysis, using a little more sulphuric acid with the hydrofluoric acid.

Carbon in Soluble Ferro-titanium.—Some ferro-titaniums of low silicon content can be completely decarbonized at 950° C. in a fused silica or tapered zirconia tube with oxygen. See Electric Combustion Furnace, page 276. It is safer to burn the sample in red lead. Burn 1 or 2 grams of thin drillings or 30-mesh powder with 2 grams of red lead.

Insoluble Ferro-titanium.—Carbon, sulphur, and phosphorus are determined as given in the analysis of soluble ferro-titanium.

Silicon and Titanium.—These elements can also be determined by fusion of 0.5 gram of the finely ground substance with 15 grams of acid potassium sulphate in a 40 c.c. platinum crucible. This fusion is highly satisfactory if conducted with a little experience. Heat the crucible very gradually at first, using the white flame of an argand burner. Keep the melt below redness until all of the water has been driven out of the flux without sputtering. When slight fumes of sulphuric anhydride begin to make their appearance the heat can be increased to low redness. Maintain this temperature until the substance is in a state of clear fusion, and is a pure yellow, free of all black specks.

If the argand burner flame is properly adjusted, this operation can be going on with only occasional attention. When all black is gone, raise the heat until fumes of sulphuric anhydride come off briskly when the lid is lifted slightly.

Then turn off the heat and run the melt well up the sides. Place the crucible in a 250 c.c. casserole with 50 c.c. of water plus 50 c.c. of 1 : 3 sulphuric acid. Dissolve with heat. Filter out the white insoluble residue; wash it free of iron and sulphate, using barium chloride solution for the latter test and KCNS for the former. Ignite it in a weighed crucible. Weigh as SiO_2 plus a little TiO_2. Evaporate with HF and a few drops of H_2SO_4 and calculate the loss of weight to silicon. Keep the non-volatile portion to add to the main portion of TiO_2.

The filtrate and washings from the silica are made nearly neutral with ammonia and precipitated with thiosulphate of soda, and finished as in soluble ferro-titanium for Ti.

Iron by Fusion with $KHSO_4$.—Fuse 0.5 gram as for silicon. Reduce with H_2S and finish as given under the soluble ferro.

Aluminum.—Proceed by fusion as given under aluminum in soluble ferro-titanium.

Manganese in Insoluble Ferro-titanium.—If the percentage of manganese is under 2 per cent, fuse 0.100 or 0.05 gram with twenty times this weight of sodium carbonate and one-fifth that amount of potassium nitrate. Dissolve the melt in a small porcelain dish with as little water as possible. Clean the platinum crucible with a little hydrochloric acid; acidulate the water solution of the melt with the same acid. Add to this solution the cleanings of the crucible and also 10 c.c. of 1 : 1 sulphuric acid. Evaporate to thick fumes. Dissolve the residue in water. When the iron sulphate is dissolved, wash the solution into a 10 by 1 inch test tube and dilute to 20 c.c. Add 10 c.c. of conc. nitric acid and finish as in steels.

For higher percentages of manganese proceed as given for high manganese in soluble ferro-titanium except that the substance is gotten into solution by a bisulphate fusion as given under the determination of silicon in insoluble ferro-titanium. Transfer the sulphuric acid solution of the melt to a liter flask and precipitate the iron and titanium with zinc oxide. Use 1 gram of sample and fuse it with 30 grams of bisulphate.

Titanium Steels.—For phosphorus, manganese, silicon, aluminum and carbon proceed as in plain steels if the titanium is present to the extent of a few tenths of a per cent.

Sulphur.—Even a few tenths of a per cent of titanium lead to low sulphur results by the evolution process. For example, where results showing 0.006 per cent by evolution were obtained, 0.012 sulphur was gotten by the ordinary gravimetric sulphur method for steels. Again, 0.075 per cent sulphur was gotten by evolution in a titanium experimental ingot when the gravimetric result was 0.11 per cent. Use either the gravimetric process by direct solution, or fuse 2 grams of sample with 20 grams of sodium carbonate plus 4 grams of niter, and proceed as in sulphur in high silicon ferro-vanadium, filtering out the sodium titanate before acidulating with HCl. Or use the author's method by evolution at 950° C. in a tapered tube (see pages 122 124).

Titanium in Steel. *Gravimetric.*—The titanium is determined gravimetrically as in nearly soluble ferro-titanium except that 4 or 5 grams of sample should be used.

Volumetric.—So far the most practical way is the well-known color method, using hydrogen peroxide. The author proceeds as follows:

Determine gravimetrically the amount of titanium in a soluble ferro-titanium containing from about 8 to 10 per cent of titanium, for use as a color standard.

Plain Titanium Steel.—*Color Method.* If the titanium content is 0.05 per cent or over, weigh 0.500 gram of drillings into a 10 by 1 inch tube. Also weigh 0.500 gram of a plain carbon steel that contains no titanium by the qualitative test. Add to the latter enough of the standard ferro-titanium to bring the amount of titanium present in this standard mixture to within about 0.05 per cent of the titanium content of the test. If the test is likely to be about 0.15 per cent Ti, then the standard should either be about 0.10 per cent Ti or 0.20 per cent Ti. The nearer the standard is to the test, in titanium content, the better.

Dissolve the drillings in 10 c.c. of dilute sulphuric acid. Add 5 c.c. of conc. nitric acid; boil off red fumes. The black insoluble matter or any insoluble matter at this stage must be filtered out; washed with 1 : 30 nitric acid; ignited free of char in a platinum crucible; fused with twenty times its weight of Na_2CO_3 plus the equal of its weight of niter; the melt dissolved out with water; acidulated with HCl; evaporated to fumes with 4 c.c. of 1 : 1 H_2SO_4; taken up with a few c.c. of water and H_2SO_4; heated until all sulphates are dissolved. This solution is then added to the main original nitric filtrate of the sample.

Transfer this solution, which should be clear, to a glass-stoppered comparison tube of about 15 to 16 mm. outside diameter and with the graduated part about 38 cm. long. Add to the solution in the comparison tube 5 or 6 c.c. of the peroxide mixture used in the qualitative Ti and V tests, page 4. Stopper the tube and mix the contents thoroughly. Transfer the test to the other comparison tube and treat it in like manner. If there is a great difference in color between standard and test, results will only be roughly approximate and the work should be repeated, preparing a new mixture of standard ferro-titanium and plain carbon steel, to imitate the test within the 0.05 limit or closer.

The following actual case will illustrate calculations, etc.:

The standard mixture consisted of 8 mg. of 8 per cent Ti ferro plus 500 mg. of a plain carbon steel of approximately the same carbon content as the sample to be tested.

The test matched the standard at 38.3 c.c. with the standard diluted to 35 c.c. Since the standard contained 8 mg. of 8 per cent ferro-titanium, its color was due to the presence of 0.008×0.08, or 0.00064 gram, of metallic titanium; therefore we have the proportion:

Stand Vol.		Test Vol				
35 c.c.	:	38.3	: :	0.00064	:	X,

or $38.3\times 0.00064\div 35=0.0007$, or 0.0007 gram of titanium found. $0.0007\times 100\div 0.5=0.14$, or 0.14 per cent titanium when 0.5 gram is taken for analysis. The gravimetric result on this sample was 0.158. Another sample gave 0.134 per cent by color and 0.140 per cent by gravimetric analysis.

For percentages as low as 0.05 per cent and under, use a gram of sample and proceed accordingly, preparing standard mixtures of similar percentage. If the titanium steel also contains not over 0.5 per cent of elements that color acid solution, such as chromium and nickel, the amounts of the latter present in the test should be determined by the rapid methods given under chromium and nickel in steel. Add to the standard enough shot nickel if titanium nickel steel is being tested, or enough potassium dichromate reduced with the least possible excess of sulphurous acid if the test be chrome-titanium steel, to exactly imitate the sample under examination, and then proceed as usual.

Qualitative Test for Titanium.—Proceed as given under Qualitative Test for Vanadium, page 4.

ANALYSES

Insoluble Ferro-titanium	Per Cent
Titanium Oxide Ti_2O_3	87.80
Silica, SiO_2	0.85
Iron Oxide, Fe_2O_3	4.64
Sulphur	0.52
Carbon	1.89
Phosphorus	0.055

Soluble Ferro-titanium	Per Cent.
Titanium	8.12
Manganese	0.58
Silicon	0.50
Iron	86.92
Aluminum	3.00
Phosphorus.	0.10
Carbon	0.26

The Determination of Titanium in Steel by Removing the Bulk of the Iron with Ammonia

This method can be used for either high or low per cents of Ti and is especially valuable for low per cents such as 0.01 to 0.05 per cent Ti. Dissolve 5 to 15 grams of the sample as far as possible in 1 : 3 sulphuric acid in the same manner as described for Al in steel (see pages 189–190). Filter out the insoluble residue of carbides. Wash the same with water until free of ferrous iron test with potassium ferricyanide.

Ash the carbide residue in a platinum crucible; fuse the ash with twenty times its weight of Na_2CO_3 plus the equal of its weight of niter. Keep molten for twenty minutes. Dissolve the fusion out in water; clean the crucible by warming in it a little HCl. Acidulate the water solution of the fusion with HCl; heat until all is in solution and add this solution to (A) before peroxidation.

To the original main filtrate and washings from the insoluble carbides add ammonia a little at a time until a slight blackish precipitate is obtained which does not redissolve on stirring; filter off this precipitate; wash it ten times with water. The bulk of the iron is thus removed. On the filter will be all of the Ti that was not filtered off with the carbide residue in the beginning. Dissolve this blackish precipitate off the filter with hot HCl 1 : 1; wash the filter paper free of iron (save the filter paper); call the solution and washings (A). (A) plus the solution of the fused carbides (already mentioned as added to (A) before peroxidation) now contains all of the Ti and Al in the steel; and also all of the Cr, V, U, and Zr.

If it is desired to get the Ti by the gravimetric method (A) is now converted to sulphate by fuming it with 50 c.c. of 1 : 3 H_2SO_4. Finish for titanium by precipitation with $Na_2S_2O_3$ as already described on pages 49 52.

Titanium in Chrome Steel, Chrome Vanadium and Tungsten Steel.—Dissolve the steel in the same manner as described for titanium in steel by removing the bulk of the iron by ammonia. When solution (A) has been combined with the solution of the carbides in the manner described, then separate the chromium by repeated peroxidations in the manner given for this separation on page 179. The iron and titanium will finally be left behind on the filter free from V, Al, and Cr. Dissolve the iron and titanium off the filter with hot 1 : 1 HCl. Ash all of the filter papers from which the hydroxides were dissolved in the different peroxidations, as there may be still some Ti remaining in them. Also ash the main iron and titanium hydroxides. Fuse the combined ashes with twenty times their weight of potassium bisulphate until a clear fusion is obtained. Dissolve this fusion out in 1 : 3 H_2SO_4, using heat to aid in the solution. When all is in clear solution dilute the clear cold solution to 500 c.c.; mix well and take aliquot parts 50 and 100 c.c. portions by means of a burette; add to each portion 5 c.c. of conc. nitric acid; boil; cool; add 5 to 10 c.c. of the peroxide solution prepared as given on page 4, and then finish by color comparison. Known amounts of made up standards should be put through all of the operations.

Also the total 500 c.c. can be finished gravimetrically.

THE DETERMINATION OF TITANIUM IN NICKEL STEEL

Suppose it is required to obtain the titanium content of a steel containing 3.60 per cent Ni: Dissolve 5 grams of the sample, as on page 63, using 75 c.c. of 1 : 3 sulphuric acid for the solution, heating in boiling water for one hour to eliminate as much as possible the carbon before adding the 25 c.c. of conc. nitric acid to accomplish the oxidation of the iron and dissolve the titanium. For a standard mixture dissolve and oxidize 5 grams of plain steel to which enough nickel ammonium sulphate has been added to equal 3.60 per cent Ni in 5 grams, and also 5 mgs. of 8.20 per cent Ti ferro-titanium. Dilute the cooled solutions of the standard and the test to the mark in 250 c.c. volumetric flasks; mix and note if the two solutions are about the same shade of brown. If the standard solution is distinctly browner prepare a new standard using a lower carbon plain carbon steel, adding the nickel sulphate and 5 mgs. standard ferro-titanium. If now there is only a slight difference in the color of the solutions due to dissolved carbon proceed with the comparisons in the manner described on page 64, using 25 c.c. from each flask. This method was used on a steel that contained 0.008 per cent Ti. However, it is better to remove the bulk of the iron with ammonia, etc. See pages 189–191.

THE DETERMINATION OF TITANIUM IN CHROMIUM-VANADIUM-NICKEL-TITANIUM-TUNGSTEN STEEL

Owing to the interference of the vanadium and the chromium, the latter must be removed. This can be best done by peroxidizing the solution of the sample and standard mixtures in the same manner as described on pages 34 35. If the chromium is considerable it will require three peroxidations at least to remove the chromium and vanadium. The redissolving and reperoxidizing must be continued until the filtrate from the iron and titanium is no longer colored yellow. The steel and standard mixtures are dissolved in 50 c.c. of 1 : 3 sulphuric acid; 0.500 gram of sample is taken for analysis. A chromium-tungsten-vanadium steel containing no nickel or titanium was used as a basis of a standard, and to it was added 35 mgs. of nickel ammonium sulphate and 5 mgs. of 8.20 per cent (Ti) ferro-titanium. After the chromium color has been removed by several peroxidations from the standard and test, the iron and titanium are dissolved off the filters with 50 c.c. of hot 1 : 1 HCl; the filter is washed free of iron; the filtrate and washings will contain all of the titanium and iron except a slight amount that may still remain on the filter, which is ashed and fused with one gram of sodium carbonate; the fusion is dissolved in 20 c.c. of 1 : 1 HCl and added to the main solution of the iron and titanium. Evaporate this latter solution to 5 or 10 c.c.; add 100 c.c. of strong nitric acid; heat with the cover on until all spraying is over and then evaporate to 5 c.c.; add 10 c.c. of water and filter into the comparison tube, washing with 1.20 nitric acid; add 10 c.c. of peroxide solution and compare. Example: Test matched the standard mixture as follows: 76.7 c.c. test equal 91.2 c.c. of standard; therefore since the standard contained 0.41 mg. Ti, 76.7 : 91.2 :: x : 0.41 mg. Ti, or 76.7 times 0.41 mg. Ti divided by 91.2 divided by 500 multiplied by 100 equals 0.068 per cent Ti. A duplicate analysis on this steel gave 0.070 per cent Ti, using 0.600 gram of sample. In the case of a similar steel that contained 0.80 per cent Ti, the nitric acid solutions containing the iron and titanium, freed as above from the V and Cr, were diluted to 250 c.c. and 50 c.c. were taken from the standard and test for the comparisons. 0.81 per cent Ti was obtained and a check of 0.78 per cent Ti. No attention is paid to the tungsten as it is removed along with the Cr and V.

CALCULATIONS

70 mg. of 8 2 per cent Ti ferro-titanium were used in the standard mixture; 61.5 c.c. of standard equal 78 c.c. of test. One-fifth of 70 mg. times 0.082 equals 1 148 mg. Ti. Therefore 61 5 78 :: 1 148 : x; x equals 1.456 mg. Ti. Now 0.9 gram was taken in this case for the analysis and one-fifth or 0.18 gram of the test was used in the comparison; hence 0.00145 gram × 100 divided by 0.18 equals 0.809 per cent Ti.

SOME FURTHER ANALYSES OF FERRO-TITANIUM

	No 1	No 2	No 3	No 4	No 5
	Per Cent	Per Cent	Per Cent	Per Cent.	Per Cent.
Carbon	7 00	1 05	0 04	3 69	1.85
Manganese	0 28	0 40	0 39	0 19	0 15
Silicon	1 08	0 64	2 51	0 42	14.90
Titanium	7 30	8 40	20 44	29 17	6 15
Aluminum	0 42	2 93	3 10	9 87	2 25
Iron	84 20	86 53	73 17	56 78	74 60
Chromium	. .		0 52	.	.....
Phosphorus		.	.	....	0 15

Chromium.—The chromium was obtained in the above No. 3 as in a steel, no attention being paid to the presence of titanium.

Analysis of Basic Slag Containing Titanium.—*Silica.*—Dissolve 1 gram of the finely ground slag, after first stirring it into a thin, smooth paste with a very little water, in a No. 5 porcelain dish in 50 c.c. of conc. HCl. Warm until solution is practically complete, evaporate to dryness and heat until very little acid can be detected when hot. Dissolve again in 30 c.c. of conc. HCl; add 100 c.c. of water; filter; wash free of iron test. Burn in a weighed platinum crucible; add a large excess of H_2SO_4, about 2 c.c. to prevent loss of Ti as fluoride and remove the silica with 15 c.c. of HF; calculate the loss of weight to silica. For extreme accuracy the solution of the slag should be evaporated twice to dryness with HCl, filtering after each evaporation and solution in HCl and water.

Oxide of Iron.—Dissolve 1 gram of the slag, as for the silica, in a 600 c.c. beaker and dilute the solution to 300 c.c.; heat to boiling; reduce with stannous chloride without separating the titanium; cool; add an excess of mercuric chloride solution and titrate with N/20 potassium dichromate as in iron ores.

Titanium Oxide.—Dissolve 1 gram, as for silica, in a liter boiling flask and dilute to 300 c.c.; make two peroxidations as described on page 49, obtaining the titanium and iron on the filter and the alumina in the combined filtrates and washings from the two peroxidations.

Oxides of Manganese, Calcium and Magnesium.—Dissolve 1 gram in 50 c.c. of conc. HCl in a 600 c.c. beaker and make two basic separations, as directed for the separation of iron from manganese on page 244, beginning at the point where the filtrate and washings are diluted to 300 c.c. The combined filtrates from the two basic acetate separations contain all the Ca, Mg, and Mn in the slag. Acidulate the combined filtrates with HCl and evaporate them, if necessary, to 400 c.c. and make the same slightly but distinctly ammoniacal. Then add slowly a water solution of potassium ferricyanide; use the c.p. salt of a clear resinous red color and free of the suggestion of bluish color, as ferricyanide containing blue material is partly decomposed as follows: $Fe(CN)_3 \cdot 3KCN = Fe(CN)_2 + CN + 3KCN$, and will not precipitate the true manganese ferricyanide but a mixture of the latter and cyanide of iron. Dissolve 3.75 grams of the potassium ferricyanide in water and dilute to 1 liter. 1 c.c. of this solution will precipitate about 0.001075 gram of manganese. $2K_3Fe(CN)_6 + 3Mn(NO_3)_2 = Mn_3[Fe(CN)_6]_2 + 6KNO_3$. Add a slight excess of the precipitant and allow the solution to stand a half hour before filtering. Mix some paper pulp with the precipitate, filter it, and wash it with a solution of 5 grams of ammonium nitrate dissolved in 500 c.c. of water made alkaline with 5 c.c. of strong ammonia. In order to secure a rapidly subsiding precipitate it is best to make the manganese solution, at first, just ammoniacal enough to turn a small piece of red litmus paper floating in it blue; then add 5 c.c. of 1 : 1 ammonia water in excess. After washing the manganese ferricyanide as described until 1 c.c. of the washings acidulated with nitric acid no longer give a chlorine test with silver nitrate, it is burned at a low red heat until free of carbon of the filter paper; it then consists of a mixture of oxides of manganese and iron which can be analyzed for manganese as usual. This mixture of oxides of manganese and iron seems to be of fairly constant percentage of manganese if always burned off at definite temperature. The author is not yet prepared to recommend weighing the mixture of oxides as a gravimetric method for manganese. He made many experiments with this in view and obtained some promising results. Where large amounts of manganese are precipitated in this way in the presence of lime, it is advisable to dissolve the mixture of oxides in 20 c.c. of conc. HCl and make a basic acetate separation of the iron; the manganese in the filtrate and washings from the iron acetate is again precipitated as before with ferricyanide and the filtrate and washings from the manganese are combined with the filtrate and washings from the original ferricyanide precipitation of the manganese. In this way the possibility of any lime being carried out with the manganese ferricyanide is obviated. This second precipitate of manganese ferricyanide is burned off with the iron from which it has just been separated, otherwise two basic acetate separations would have to be made at this point instead of one. The total ash contains all of the manganese freed from the lime and magnesia. The manganese can now be dissolved and determined as on page 244. (See also page 345.)

* *Lime and Magnesia.*—The combined filtrates from the two manganese ferricyanide precipitations are treated with 100 c.c. of conc. nitric acid and evaporated to dryness. This acid should be added to the solution before the evaporation begins, to prevent as far as possible, the formation of the blue cyanides. When the evaporating solution reaches a certain degree of concentration

it should be watched as spraying may begin, and at this stage the casserole should be covered until this action is over; the cover is then removed and the evaporation continued to dryness. The residue in the casserole is taken up with 100 c.c. of HCl and concentrated to 20 c.c. after the action between the acid and the salts is over. Add 100 c.c. of water; and precipitate the iron with ammonia; filter; wash with water until the washings are freed of chloride test obtaining filtrate (A). Redissolve the iron hydrate; and precipitate it again; filter; wash; and combine the filtrate and washings with (A). The combined filtrates and washings are made faintly ammoniacal and the calcium is precipitated with ammonium oxalate as in the analysis of limestone. The oxalate is filtered, washed, and reprecipitated. The two filtrates from the oxalate are combined and the magnesium is precipitated as given on page 433.

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* See also pages 135–137 for the separation of Mn from CaO and MgO by means of ammonium persulphate.

Phosphorus.—Weigh 0.500 gram of the slag into a porcelain dish and with it an equal amount of potassium chlorate; moisten to a thin paste with water and then pour in 50 c.c. of conc. HCl. Heat until all is in solution except the silicic acid, remove the cover and evaporate to dryness but not at a baking heat. Redissolve with 30 c.c. of conc. HCl; and add 50 c.c. of water; filter; wash; convert to nitrates by evaporating twice to 20 c.c. with 50 c.c. of conc. nitric acid; boil with a slight excess of $KMnO_4$ and finish as for phosphorus in steel.

THE ANALYSIS FOUND

	Per Cent		Per Cent
SiO_2	19 45	MgO	5 80
FeO	6 75	MnO	9 00
Al_2O_3	1 05	TiO_2	5 63
CaO	47 66	P_2O_5	4 39

CHAPTER IV

PART I

ANALYSIS OF TUNGSTEN POWDER

FUSE 0.6 gram of the powder with a mixture of 10 grams of carbonate of soda well ground in a mortar with 2 grams of potassium nitrate. A complete fusion is obtained in twenty minutes. The melt is dissolved with water in a platinum dish. It is transferred to a 300 c.c. casserole and acidulated with hydrochloric acid—keeping the dish covered during acidulation. The solution is heated for a half hour with cover on, or until all danger of loss by spraying is over. The cover is removed and the acidulated fusion is evaporated to dryness. 10 c.c. of 1 : 1 hydrochloric acid are then added and the contents warmed until iron is dissolved. 200 c.c. of water are next put into the dish, and the solution is heated for thirty minutes to dissolve all sodium salts.

The precipitated tungstic acid is filtered out and washed free from iron test with very dilute hydrochloric acid. It is washed twenty more times to insure removal of salts. The filtrate and washings are again evaporated to dryness, dissolved, filtered, and washed as before. The second filtrate and washings are treated with a hydrochloric acid solution of cinchonine to remove the last traces of tungstic acid. (See page 131.)

The three portions of the tungsten are burned off at a low red heat until bright yellow. This yellow residue is weighed; moistened with a few drops of sulphuric acid; 15 c.c. of HF are added cautiously. (If the operator by accident spills any of the latter acid on himself he should lose no time in soaking the part with ammonia. HF left in contact with the skin for any time causes burns that are very liable to produce infected slowly healing sores.) Evaporate to fumes in a good draught; ignite cautiously, heating the crucible from the top down until it very gradually reaches a low red heat. Do not blast, as tungsten oxide is slowly volatile at high heats. Weigh again. The difference or loss of weight from the first weight is the silica. Silicon does not exist in the elemental form in tungsten powder made by reduction at 1100° to 1200° C. If the sample being analyzed is crushed ferro-tungsten, then the loss of weight can be properly calculated to silicon by use of the factor .4693.

Tungsten. The residue remaining in the crucible contains all of the tungsten, together with a little of the iron. It is fused with 20 grams of sodium carbonate at a bright red heat until all bubbling is over and the melt is in a state of quiet fusion. Dissolve the fusion in water, in platinum or platinum substitute dish. If a platinum dish is not available, a casserole or porcelain evaporating dish can be used. Warm gently just long enough to insure a complete fusion. Avoid long heating and boiling, especially if a porcelain vessel is used, as it is liable to be attacked. When the water insoluble residue is light and floats around, the extraction of the sodium tungstate, etc., is complete. If the supernatant liquid is greenish, due to presence of manganate, heat the extraction with a few drops of alcohol.

When the green color is gone, all of the manganese is precipitated, and the insoluble residue can be filtered out, and washed thoroughly with water, mixing a little paper pulp in with the extraction before it is filtered. It will take sixty washings to insure the complete washing out of the carbonate of sodium.

This washed, water-insoluble residue will contain mainly iron oxide in the powders of about 95 per cent tungsten, but if the residue exceeds a few milligrams, it should be ashed in the same crucible, weighed, and fused with twenty times its weight of Na_2CO_3; extracted with water; filtered; washed with water; ignited, and weighed; its weight deducted from the first weight of the WO_3. The remainder is the weight of the total pure WO_3 plus any oxides of tin, aluminum, and molybdenum that may have been weighed with the WO_3, making the tungsten result too high unless corrected for.

To correct for the Sn, Al, etc., make the two sodium carbonate filtrates and washings acid with HCl; then just ammoniacal. Any Al, Ta, Nb, Sn that have gone into solution will now be precipitated. Filter off the flocculent precipitate, if any; mix in a little paper pulp before filtering, wash it at least sixty times with water containing 5 grams of NH_4NO_3 per 500 c.c. Ignite it; weigh it and deduct the weight from total weight of the first crude silica-free WO_3, after first deducting the double fused iron oxide as before described. If the ammonia precipitate weighs more than a milligram or two, it may contain some tungsten, consequently the deduction for Al, etc., will have been too great and this precipitate must also be fused with twenty times its weight of Na_2CO_3; acidulated with HCl; heated until all is in clear solution and cinchonine added to the only moderately acid solution. This solution should be allowed to stand over until the next day. If any precipitate forms it is tungsten, and must be filtered off; washed with cinchonine at least sixty times; ignited; weighed, and *added* to remainder obtained after deducting from the first crude WO_3, the double fused iron and manganese oxides and the crude Al_2O_3, SnO_2, etc., before mentioned. This net amount will be the weight of the pure WO_3 plus any MoO_3 that may have been present. To correct for the MoO_3, the ammoniacal filtrate from the crude Al_2O_3 plus SnO_2, etc., is treated with 4 grams of tartaric acid to hold the tungsten in solution. It is then made *slightly* acid with HCl and saturated with H_2S.

Any brown precipitate is filtered off; washed with H_2S water at least sixty times; ignited in a porcelain crucible at the lowest possible heat—just below redness; then the heat raised slightly, if necessary, to burn out all of the paper char. Weigh this residue, which will be a whitish ash unless some copper be present, when it will persist as a blackish residue. Deduct its weight from net amount of the pure WO_3 plus MoO_3, and the remainder will be the final weight of the pure WO_3, from which the W is obtained by the factor 79.31. This product divided by the weight taken gives the per cent of tungsten in the sample.

Rapid Method for Tungsten.—Weigh 1 gram of metal into a platinum dish.* Add 10 c.c. of pure hydrofluoric acid. Cover with a lid. Warm in a good draught. Remove from fire. Add three or four drops of conc. nitric acid. Violent action occurs at this point. Continue to add nitric acid a drop at a time until further additions of acid produce no action. This will take, in all, about 5 c.c. of conc. nitric acid. Remove the lid, rinsing off its surface, permitting the washings to flow into it. Add 10 c.c. conc. sulphuric acid. Evaporate to thick fumes of SO_3. Cool, moisten with 10 c.c. of conc. hydrochloric acid. Add 10 c.c. of water, transfer the contents of the dish to a 600 c.c. casserole, and heat to boiling with constant stirring to prevent bumping. Cool. Filter. Wash with 1 : 10 hydrochloric acid until free of iron test. Ignite and weigh the tungstic acid as trioxide. Fuse the latter with sodium carbonate and finish as in the first method. This rapid scheme is a modification of Arnold and Ibbotson's method. (See, Arnold and Ibbotson's "Steel Works" Analysis, 1907.)

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* Or a platinum substitute dish, of which there are several kinds that will answer for such work.

IRON AND SULPHUR IN TUNGSTEN POWDER AND FERRO-TUNGSTEN

Iron.—Fuse the finely ground sample in a powdered mixture of 20 grams of sodium carbonate and 4 grams of niter. Dissolve the mixture out in water in a porcelain dish or casserole. Clean the crucible with a little HCl until all stains are gone. Rinse all cleanings into the dish Acidulate the fusion with HCl and evaporate the contents of the dish to dryness, but do not bake. Take up in HCl and water, heating until all salts are in solution.

Filter out all separated tungsten trioxide. Wash thoroughly with HCl wash water. Evaporate filtrate and washings again to dryness. Take up as before; filter and wash. Combine the two sets of filtrates and washings which will contain the bulk of the iron and all of the sulphur. Burn off the two residues on the two filter papers until free of paper char. The ash will contain the bulk of the tungsten present and a little of the iron. To obtain this part of the iron the ash must be fused with twenty times its weight of sodium carbonate until a quiet fusion is obtained. This should be done at a bright red heat.

Dissolve the melt out in water in a casserole as in the first fusion. When the small brown residue floats around, it is well extracted and can be filtered off. Washed thoroughly with sodium carbonate water and then with water alone. To insure the complete removal of the tungsten, which is essential, the ignited residue should be fused again as before; dissolved out in water; filtered off; washed with water thoroughly; then dissolved off the filter with hot HCl; the filter washed free of iron test, and the filtrate and washings added to the two sets of filtrates and washings which were previously mentioned as containing the bulk of the iron and all of the sulphur. This total combination of filtrates and washings will contain all of the iron and sulphur and some tungstic acid still in solution. Make these filtrates, etc., slightly ammoniacal; heat; filter out the iron; wash it thoroughly with water. Keep the filtrate and washings for the total sulphur. Ignite the washed iron hydroxide; dissolve it out with HCl; pour the solution into dish; rinse the crucible out well into the dish; evaporate all to dryness; take up in the least amount of water and acid; heating until all is in clear solution except some yellow precipitate of tungstic acid that is almost certain to separate out here. This must be filtered out; washed; the filtrate and washings evaporated to fumes with about 30 c.c. of 1 : 3 H_2SO_4 taken up by heating with some water and about 10 c.c. more of the sulphuric acid.

This should be again filtered if it shows any turbidity of tungstic acid; the filter washed free of iron test with sulphuric wash. The filtrate and washings should now be free of tungsten and contain the total iron. Evaporate to 100 c.c. volume and pass the solution through the zinc reductor and titrate with the permanganate standard used for the determination of iron in graphites if the percentage of iron is small as in a powder, but if the sample is a ferro an aliquot part of the solution should be reduced and titrated with the permanganate standard of the strength used in iron ore. (See page 39.)

Sulphur.—The filtrate and washings last referred as to be kept for the total sulphur should be treated with a cinchonine solution, using 20 c.c. of the solution, which is made by dissolving 25 grams of cinchonine in 200 c.c. of 1 : 1 HCl. Let the solution of this sample stand several hours after being treated with the 20 c.c. of the cinchonine. If any precipitate forms, it must be filtered off and washed with a wash consisting of 10 c.c. of cinchonine solution dissolved in 500 c.c. of water. Heat the filtrate and washings and add about 30 c.c. of a saturated solution of barium chloride. Let stand overnight, and finish for sulphur as in plain steels, weighing the barium sulphate. (See page 335.)

Total Sulphur by Evolution.—The best and easiest way to get the total sulphur in tungsten powder, ferro-tungsten, oxide, etc., is to heat 1 gram or less of the substance in the finely powdered state in a tapered clay combustion tube at a temperature of 950° C. in a stream of hydrogen saturated with HCl. The evolved H_2S is caught in an ammoniacal solution of cadmium chloride and finished exactly as in plain carbon steel. (See pages 122–129.) In this same way the total sulphur is evolved from such sulphates as $BaSO_4$ Na_2SO_4, $CaSO_4$, as hydrogen sulphide, by the following reaction:

$$BaSO_4+2HCl+8H=BaCl_2+H_2S+4H_2O.$$

Blanks.—Blanks must be run for iron, and sulphur on the same amounts of all chemicals and acids used, and for silica, and deducted. The reagents are almost certain to be contaminated with all of these elements.

It has been pointed out that sodium carbonate may contain enough iron to make an appreciable error in the tungsten determination by reason of deducting from the crude WO_3, not only the iron that existed in the same but also that which contaminated the sodium carbonate used in the fusion. The remedy is to subtract the amount of iron and alumina in the carbonate from the total iron and alumina found, before deducting the latter from the crude WO_3. Credit is due to Mr. Geo. M. Berry for emphasizing this point, which is one phase of the general necessity of running blanks on all reagents that one uses for any analysis whatsoever.

Phosphorus.—The author has found that the practice of decomposing tungsten-bearing materials by fusing them with a mixture of sodium carbonate and potassium nitrate, leaching out the fusion, acidulating with hydrochloric acid, removing the tungstic acid by several evaporations to dryness, and then using the filtrate and washings from the tungstic acid for the determination of the phosphorus, gives far less than the actual per cent.

The method that he now uses together with the proof of the accuracy of the same, he first published in the Journal of Ind. and Eng. Chem., Vol. V, No. 4. The full description of his method can be found on pages 90–93.

Manganese.—Fuse 0.100 gram with 2 grams sodium carbonate and 0.5 gram of niter. Remove tungsten by one evaporation to dryness. Dissolve in 5 c.c. 1 : 1 hydrochloric acid; filter; wash; evaporate to fumes with 10 c.c. 1 : 3 sulphuric acid. Dissolve in 10 c.c. of water; wash into a 10 by 1 inch tube; dilute to 20 c.c. with water. Add 10 c.c. concentrated nitric and finish as in steels. Accurate to 2 per cent if 0.050 gram is taken for analysis when the manganese exceeds 1 per cent.

For higher per cents of manganese fuse 1 gram and remove tungsten by one evaporation. Convert the filtrate into sulphate; rinse it into a liter flask and proceed as given for high manganese in above 2.00 per cent Mn. (See page 345.)

Molybdenum in Tungsten Powders.—Fuse 1 gram as for tungsten. Dissolve the melt in as little water as possible. Filter. Wash with sodium carbonate water. Add to the filtrate and washings 4 grams of tartaric acid. Then make the filtrate very slightly acid with hydrochloric acid. Warm. Pass H_2S for an hour, or until the brown sulphide settles well. Filter off the sulphide. Wash it thoroughly with H_2S water. Ignite the precipitate at a very low heat 550° C. until white or bluish white. If it looks yellow, fuse it with a little sodium carbonate; dissolve the melt in water; add a crystal of tartaric acid and proceed as before with H_2S.

When the bluish white molybdenum trioxide is obtained, multiply its weight by 0.6666 after deducting the silica, etc. (See Molybdenum in Steel.) The methods given for tungsten powder apply also to ferro-tungsten.

Magnesia and Lime in Ferro-tungsten and Tungsten Powder.—Weigh 1 gram of sample in 3-inch platinum dish with platinum cover or in a palladium-gold substitute dish. Add 10 c.c. hydrofluoric acid and warm. Using a glass tube of moderate bore, add conc. nitric acid, drop at a time, keeping the dish covered as much as possible because of brisk action taking place, until no further action is observed.

Add about 1 c.c. HNO_3 in excess, remove lid and rinse thoroughly with distilled water; then add 10 c.c. H_2SO_4 (1.84 sp. gr.) by distributing it in drops over the contents of the dish, which should become clear due to perfect solution.

Place dish on graphite bath over moderate flame at first; evaporate low, at which stage yellow tungsten trioxide precipitates; increase flame under bath and take to heavy SO_3 fumes; cool; cover with a watch glass; then add 25 c.c. HCl (1 : 1), small quantity at a time because of violent action.

Heat for twenty minutes on graphite bath with moderate flame, dilute to about 100 c.c. with distilled water; stir for a few minutes; then transfer contents to clean 400 c.c. beaker.

Rinse dish with 1/10 HCl, wash, removing any adhering tungstic oxide, using a little ammonia in the dish for the purpose if necessary. Volume in beaker, about 150 c.c. Heat for about ten minutes on bath with occasional stirring, to insure solution of all soluble salts. Filter on double 11 cm. ashless filters, and wash fifty times with 1/20 HCl wash. The tungsten precipitate is quantitative. It should be burned off to free it from the paper; fused with 10 grams of sodium carbonate; dissolved out in water; the water-insoluble filtered out, first warming it with alcohol if there is any green manganate present; wash the filter thoroughly with carbonate water; then dissolve the water-insoluble off the filter with some hot 1 : 1 HCl, as it may contain some lime, manganese, and magnesia; wash the filter; add the filtrate and washings to the main filtrate from the tungsten. This main filtrate will now contain all of the lime, manganese, and magnesia and iron in the sample.

The whole of the filtrate may be used for the lime and magnesia, or it may be divided as follows: After diluting to 500 c.c. and thoroughly mixing the dilution:

50 c.c. = 100 mg. for manganese;
200 c.c. = 400 mg. for cinchonine pptn. of traces of tungsten;
250 c.c. = 500 mg. for lime and magnesia.

Lime.—Make the total filtrate from the tungsten to which the solution of the iron, etc., from the crude WO_3 has been added as described, slightly ammoniacal. Boil two minutes; filter off the iron, etc.; wash it with water; redissolve it in hot 1 : 1 HCl; wash the paper from which it was dissolved free of iron test. Reprecipitate the iron as before with a slight excess of ammonia; filter; wash with water. Combine the two filtrates and washings from the two ammonia precipitations. Make the combined filtrates slightly acid with HCl; evaporate to about 250 c.c. Add 20 c.c. of a saturated solution of ammonium oxalate to the evaporated solution; make slightly ammoniacal; heat to boiling. Let stand several hours, preferably overnight.

Filter on double 9 cm. paper, catching filtrate in 800 c.c. beaker. Wash until free of chlorides, with ammonium oxalate wash (10 c.c. saturated solution of ammonium oxalate to 500 c.c. water). Burn off with a low flame in a weighed platinum crucible;

then increase flame; finally, using blast lamp to constant weight. Weigh as CaO.

To free from traces of WO_3 and SiO_2 dissolve residue in crucible in 10 c.c. 1 : 1 HCl; filter on a small paper; wash with 1/10 HCl wash; burn off; weigh and deduct.

Reprecipitate the lime in this filtrate as before; wash it; weigh it again as a check. The oxalate filtrates and washings from the two lime precipitations should be combined for magnesia.

Magnesia.—Evaporate these two filtrates and washings to about 500 c.c. volume. Add 20 c.c. of a saturated solution of sodium ammonium phosphate. Stir and add 150 c.c. ammonia (0.90 sp. gr.). Let stand overnight; filter on double 9 cm. paper, washing free of chloride with the following wash; 10 c.c. ammonium nitrate, 50 c.c ammonia (0.90 sp. gr.), diluted to 500 c.c. with distilled water. Burn off in a weighed platinum crucible over a low flame. When black particles have disappeared raise the flame and burn until white. If discolored, purify as directed under lime. Residue is weighed as $Mg_2P_2O_7$. Multiply by 36.20 to calculate to percentage of MgO.

Run blanks on all of the foregoing.

Carbon.—The carbon in tungsten powders can be determined by burning the latter in the electrically heated furnace without any aid to the combustion other than the oxygen. The heating in the stream of oxygen should be continued for forty-five minutes. Ferro-tungsten should be as finely powdered as possible. It is mixed with four times its weight of red lead or peroxide of lead to insure complete combustion and the burning should be continued for thirty minutes at least. Blanks must be determined on the oxide of lead used, and deducted from the total CO_2 found. (See Chapter XI, page 257.)

Sulphur by Fusion in an Iron Crucible.—Sulphur can be very accurately determined by fusing in an iron crucible 1 gram of the tungsten powder or the ferro-tungsten with 15 grams of sodium peroxide mixed with 7 grams of sodium carbonate.

The melt is dissolved out in water, in a casserole, and evaporated to dryness after adding an excess of HCl. Proceed from this point to remove the tungsten, as given on page 76, until the last traces of it have been precipitated with cinchonine. The filtrate from the cinchonine tungstate is then precipitated with barium chloride and the sulphur finished as given for steels (page 335). Run complete blanks including every operation. If the cinchonine contains excessive amounts of sulphates, as is sometimes the case, these can be removed by washing the crystals on a porcelain colander with distilled water until the washings no longer give a precipitation with barium chloride solution. This may cause some loss of the cinchonine. A sulphur determination of any tungsten compound should, without fail, have this cinchonine treatment to remove last traces of the metatungstate, otherwise the latter tungstate will contaminate the barium sulphate, frequently causing serious error. See also evolution method in a hot tube in a stream of hydrogen and HCl vapor, at 950° C. (See page 122.)

THE DETERMINATION OF OXYGEN IN METALLIC TUNGSTEN POWDER AND SOME NOTES ON THE DETERMINATION OF OXYGEN IN STEEL

It has been found a distinct advantage both in the manufacture and use of tungsten powders to know their oxygen content. In one of the laboratories under the author's direction, this determination is a matter of daily routine. The method involves the same principle used in the determination of oxygen in steel, i.e., the ignition of the substance in a stream of hydrogen, which method is credited to Ledebur.

The electrically heated furnace introduced by the author * in 1908 for the direct determination of carbon in iron, steel and alloys is utilized in the process which is described in detail in this paper.

Walker and Patrick,† in a paper read at the Eighth International Congress of Applied Chemistry, attack the accuracy of the Ledebur method on the ground that any oxides of manganese or silicon present in the steel would not be reduced. The author regards the Ledebur method as more practical than the proposed new one † above noted; even if the former process does not reveal the total oxygen present it certainly shows

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* J. Am. Chem. Soc., 30, 773.

† Proc. 8th Intern. Cong. Appl. Chem., 21, 139; also Ind. and Eng. Chem., 4, 799.

enough of it to furnish a basis for judgment of the quality of the steel. If the steel is sufficiently dirty and poorly melted in actual, open-hearth, Bessemer, or crucible practice to contain oxides of manganese and silicon, then it would surely contain enough oxide of iron to condemn it.

The arrangement of apparatus is indicated in the drawing and the accompanying notes. The towers (or jars), page 85, are the author's design, as are also *J*, *I* and *C*, and were used first as part of a combustion train.* In this laboratory four furnaces are placed side by side. By the use of a Y tube at the outlet of jar *F*, Fig. 1, one train from *F* to *K* can be made to serve two furnaces.† Of course, a separate set of *A*, *B* and *C* is necessary for each furnace. If, after making a large number of determinations, the blank begins to show a gradual increase, the contents of the various jars must be renewed.

Method.—*Blank.*—Before introducing anything into the electric furnace, close all points marked "screw pinchcock." At *B*, Fig. 1, make a connection with a straight glass tube instead of the U tube shown. Insert quickly into the quartz tube (at the point marked *E*) the porcelain boat that has been kept at 105° C. in an air bath. Push the boat into the center of the furnace with a heavy copper wire which is marked to show how to place the boat in the hottest part of the furnace. Stopper the tube as quickly and tightly as possible. Open all four pinchcocks and turn on the hydrogen slowly until it passes through the apparatus at the rate of about seventy bubbles per minute. Allow the hydrogen to pass through the cold furnace for thirty minutes. Close all the pinchcocks and replace the glass tube at *B* by the U tube. Open all cocks and let hydrogen run for another half hour to fill the weighing apparatus with this gas. Close all pinchcocks and the glass cocks on the U tube. Remove the U tube and weigh it quickly. Insert the U tube again, open all cocks and start the hydrogen flow; turn on the electric current in the furnace and bring up the temperature to 950° to 1000° C. After reaching this temperature keep the heat on for two hours with the hydrogen passing continually. Close all pinchcocks, shut off the hydrogen, and close the glass cocks on

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* J. Am. Chem. Soc., 28, 862.

† See photo No. 1.

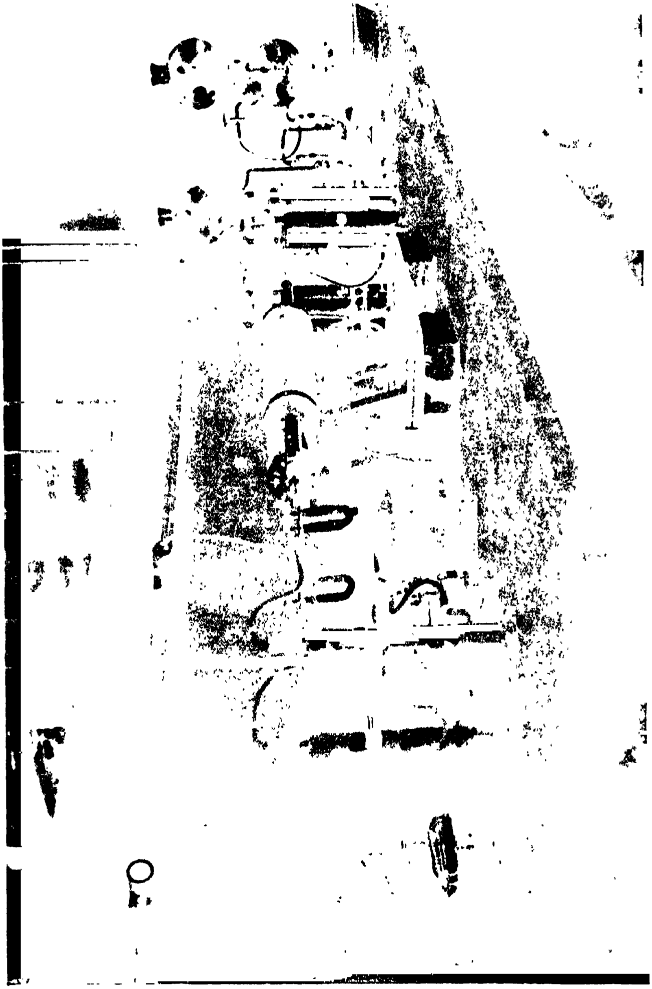

PHOTO NO. 1.

the weighing apparatus *B*. Detach and weigh *B*. The difference between this weight and the first weight represents the blank to be deducted from all determinations.

Sample.—Dry the finely ground powder of the tungsten metal to constant weight at 105° C. Put 2 or 3 grams of the powder into a porcelain boat that has been dried at 105° C. Place this in the cold furnace and stopper tightly at *E*. Using the glass tube connections at *B*, open the pinchcocks and allow hydrogen to pass through the cold furnace for one-half hour to remove whatever air entered when the charge was inserted. Close all pinchcocks and replace the glass tube by the weighed U tube at *B*. Open all cocks, adjust the hydrogen flow to seventy bubbles per minute and turn on the electric current, heating the furnace to from 950° to 1000° C. Maintain this temperature for two hours with the hydrogen passing. Close all cocks and turn off the hydrogen. Remove and weigh the U tube. The increase in weight minus the blank gives the amount of water formed by the reduction of the metallic oxides to metal. This result multiplied by 16 and divided by 18.016 is equivalent to the weight of oxygen which is converted into percentage by the usual calculations.

Standardization of Apparatus.—*With C.P. Tungstic Oxide.*—This material is prepared as follows: Treat 5 grams of 96 to 98 per cent tungsten powder in a platinum dish with 10 c.c. c.p. hydrofluoric acid. Pour on this mixture very slowly 30 c.c. of concentrated nitric acid. This produces considerable heat, and the material is dissolved as clear as water. Now add 15 c.c. of concentrated sulphuric acid, evaporate to thick fumes, cool, add from 10 to 20 c.c. c.p. hydrochloric acid, boil, from three to four minutes, add 50 c.c. of water, heat, filter, and wash free from iron and sulphates by decantation in a 600 c.c. beaker. Transfer to a platinum dish, ignite at a bright red heat in a muffle, and put in a glass-stoppered bottle. Before using any of this material for a test, ignite a portion of it at a blast lamp temperature. Immediately after the blasting put 1 gram of the oxide in a porcelain boat dried at 105° C., and charge it at once into the furnace. It will require at least six hours treatment at 950° to 1000° C. to reduce this amount of oxide and carry all of the water formed over into the weighing apparatus.

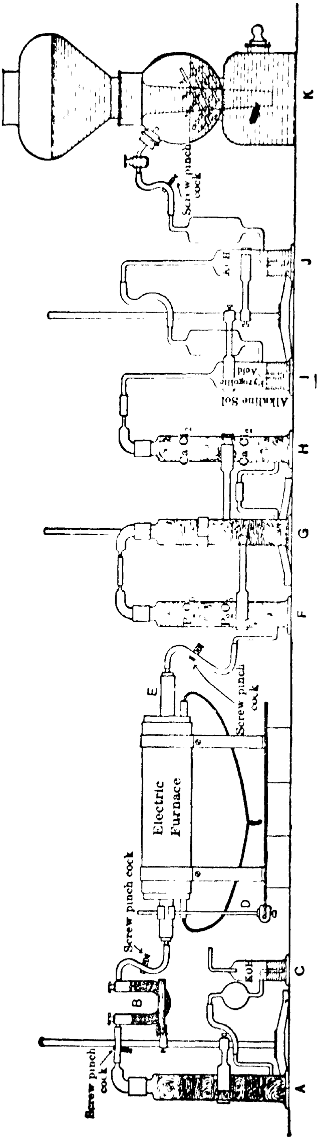
A
Screw pinch cock
B
Screw pinch cock
C
KOH
D
Electric Furnace
Screw pinch cock
E
Screw pinch cock
F
P_2O_5
P_2O_5
G
H
$CaCl_2$
$CaCl_2$
I
Alkaline Sol
Pyrogallic Acid
J
Screw pinch cock
K

FIG. 1.

With Ferric Oxide.—Dissolve 10 grams of low carbon steel of very low phosphorus, sulphur, and silicon content in 100 c.c. hydrochloric acid in a liter beaker. Transfer this to a No. 7 porcelain dish and evaporate to 10 c.c. Add 100 c.c. nitric acid and evaporate to 20 c.c. Add 50 c.c. of concentrated nitric acid, and evaporate to dryness. Place the dish in a muffle and heat to redness. Cool, dissolve in 50 c.c. hydrochloric acid, add 50 c.c. of water, evaporate to small volume, filter out insoluble matter, such as silicic acid, and precipitate with filtered ammonia. Wash the precipitate by decantation until free from chlorides, dry in a porcelain dish, heat to redness and place in a stoppered bottle. Blast a portion of this for three or four minutes, transfer 1 gram quickly to a porcelain boat, and place at once in the reduction furnace. Pass hydrogen for six hours after the furnace reaches 950° to 1000° C.

TABLE I—RESULTS OBTAINED BY APPARATUS DESCRIBED

Pure WO_3, contains 20 69 per cent oxygen.
1 gram gave 20 70 per cent oxygen.
0 250 gram gave 20 80 per cent oxygen.
0 500 gram gave 20 30 per cent oxygen.
Average, 20 60 per cent plus
Pure Fe_2O_3, contains 30 06 per cent oxygen.
0 500 gram gave 30 16 per cent oxygen.
Blanks, 0 0030 and 0 0036.

The Effect of Free Carbon on the Method.—It is an advantage to have some excess of free carbon in finished tungsten powder, and, at times, in the process of manufacture, it is necessary to know the amount of oxygen present in a powder that contains as much as 3 or 4 per cent of charcoal. Some tests were made to see if the reaction $WO_3+3C=W+3CO$ might not occur at the same time with the desired reaction $WO_3+6H=W+3H_2O$. Table II shows that the presence of excessive amounts of free carbon caused no material error in the case of the pure tungsten oxide, but did cause low results when the carbon content exceeded 5 per cent in the iron oxide. A curious feature is that 30 per cent of free carbon caused practically no lower result than the addition of 10 per cent.

TABLE II—RESULTS OBTAINED WITH MIXTURES OF OXIDES AND CHARCOAL

Grams of Mixture		Percentage Oxygen, Theoretical	Percentage Oxygen, Found	Percentage Carbon Present
WO_3	Charcoal			
0.544	0.201	20.69	20.57	26.6
0.300	0.090	20.69	19.80	23.0
0.400	0.080	20.69	20.32	16.7
0.500	0.060	20.69	20.53	10.7
Fe_2O_3				
0.5785	0.000	30.06	29.84	None
0.473	0.208	30.06	27.35	30.5
0.400	0.122	30.06	28.68	23.3
0.300	0.089	30.06	27.53	23.0
0.500	0.025	30.06	29.95	4.7
0.500	0.050	30.06	27.82	9.7

The following table shows the amounts of oxygen found in the various brands of tungsten powders made both in the U. S. and abroad. Each numeral represents a different make.

The reduction was particularly poor in the second lot received from the German manufacturer designated as II (No. 2 in his second shipment). When so much oxide is present it can be easily detected by the eye, being equivalent to 10.92 per cent of tungstic oxide. Such so-called metal has a distinct brown color.

TABLE III

Make	Imported or Domestic	Oxygen Found	Consignment
		Per Cent	
I . .	German	1.02	
II	German	1.10	No. 1
II	German	2.26	No. 2
III . .	German	0.18	
IV . .	German	0.53	
V	American	0.37	No. 1
V	American	0.47	No. 2
V	American	1.24	No. 3
VI	American	0.80	
VII	American	0.45	
VII . . .	American	0.08	
VII .	American	0.07	

The Decarbonization of Steel When Ignited in a Stream of Hydrogen for the Oxygen Test.—In 1909 the writer called attention to the fact that hydrogen will produce a bark, or decarbonized surface, on steels when the latter are heated in a current of this gas. Supplementing this statement * the following tests were made on three steels that were analyzed for oxygen:

TABLE IV

	Grams of Drillings Taken for the Oxygen Test	No. of Hours Ignited in Hydrogen	Percentage Carbon Content	
			Before Ignition	After Ignition
Sample I	9.6	3½	1.04	0.90
Sample II	16.0	3½	1.08	0.83
Sample III	19.5	3½	0.83	0.70

In the foregoing method no preheating furnace or tube is used such as was recommended by Ledebur in his "Leitfaden für Eisenhütten-Laboratorien" and adopted by others who have since written on this or similar subjects, thus simplifying matters to that extent. Also, concentrated sulphuric acid is omitted, entirely, eliminating the possibility of unpleasant, not to say dangerous, accidents from this source.

The introduction of an alkaline solution of pyrogallol into the purifying train was made at the suggestion of Mr. Simon Lubowsky, in July, 1912, when working under the author's direction. The latter adopted his suggestion as did Mr. McMillen,† of The Crescent Steel Works, who was the first to apply the electrically heated furnace, introduced by the writer, to the determination of oxygen.

Photo No. 2 shows a battery of four of the writer's furnaces which he designed some years ago and published in the Met. and Chem. Eng. The construction is very simple, consisting of a split-heat insulating cylindrical muffle, of infusorial earth; a heating element of nichrome wire wound on a collapsible

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* See "The Formation of White Scale on Steel and the Surface Decarbonization of Pipe-annealed Steel," page 423.

† Met. and Chem. Eng., 11, No. 2; also J. Ind. and Eng. Chem., Feb., 1913.

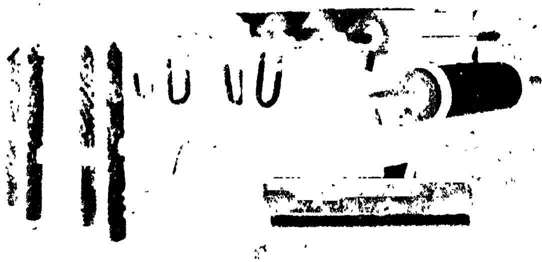

PHOTO NO. 2.

mandrel, and covered with alundum cement. These furnaces are arranged in a suitable train for the determination of oxygen in tungsten powder or in steel.

The Preparation of the Steel Sample for the Determination of Oxygen.—The steel should be first thoroughly ground and polished free of all rust and scale as a very small particle of either oxide would seriously impair the accuracy of the work. The drill should be also free of rust, grease, and scale. The drilling should be proceeded with slowly so as not to overheat the sample as this will cause oxidation. Any blue- or gold-colored drillings present indicate overheating during the drilling or milling of the samples and any such should be rejected. The coarse drillings are also rejected; and only those drillings that will pass a 20-mesh screen and will not pass a 30-mesh one are used, unless the drillings are very thin. Ten to 20 grams of sample are taken and the work is carried out as in the tungsten powder. The drillings are kept over anhydrous calcium chloride until used. The great danger about the whole operation is that improper sampling may cause oxygen to be found that does not exist in the steel. The drillings are heated at 950° to 1000° C. for two hours in the apparatus shown on pages 85 and 89, Fig. 1. and photo No. 2.

THE DETERMINATION OF PHOSPHORUS IN FERRO-TUNGSTEN METALLIC TUNGSTEN POWDER, TUNGSTEN OXIDE AND TUNGSTIC ACID BY DIRECT SOLUTION

The author found in the course of an investigation that the practice of decomposing tungsten-bearing materials by fusing them with a mixture of sodium carbonate and potassium nitrate, leaching out the fusion, acidulating with hydrochloric acid, removing the tungstic acid by several evaporations to dryness, and then using the filtrate and washings from the tungstic acid for the determination of the phosphorus, gave far less of the latter element than was actually present. He then devised the following method which he has found to give near enough to the true phosphorus for technical purposes

Phosphorus in Ferro-tungsten.—Add 30 c.c. of concentrated nitric acid to 1 gram of the powdered sample, in a platinum dish; then add slowly 3 c.c. of c.p. hydrofluoric acid. Keep the dish covered with a watch glass; warm the mixture. After warming and slight boiling, the material should dissolve to a clear solution. Transfer the solution to a No. 5 porcelain dish and evaporate to dryness; do not bake, as there is danger of losing phosphorus at this point. Dissolve this residue with 50 c.c. of concentrated hydrochloric acid. Heat with the lid on; then remove the lid and evaporate to dryness; do not bake. Dissolve again, using 20 c.c. of concentrated hydrochloric acid; heat; add 50 c.c. of water, stir, heat, and filter out the main tungsten; wash with one part of concentrated hydrochloric acid diluted with twenty parts of water. Evaporate the filtrate and washings to 10 c.c., add 20 c.c. of water, stir, and filter as before. Evaporate to 10 c.c., add 75 c.c. of concentrated nitric acid and heat with the cover on until all action is over; remove the lid and evaporate to 20 c.c. Add 50 c.c. of nitric acid, and evaporate to 15 c.c. Add 20 c.c. of water, stir, heat, and filter into a 6 oz. beaker; wash with 2 c.c. of concentrated nitric acid diluted with 100 c.c. of water, washing fifteen times. Evaporate the filtrate and washings in the beaker to 40 c.c. Replace the lid

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[1] See J. Ind. Eng. Chem., Feb. 7, 1913.

and add a slight excess of 5 per cent solution of potassium permanganate; boil three or four minutes. Dissolve the excess of manganese oxide with a little ferrous sulphate, and precipitate the phosphorus with molybdate solution.

When dissolving ferro-tungsten in the mixture of nitric and hydrofluoric acids, a porcelain dish can be used, but a little more hydrofluoric acid may be needed to secure complete solution of the alloy on account of the tendency of the latter acid to attack the dish. Further, when a porcelain dish is used, blanks must be run, using a standard steel. The latter is dissolved in the *mixture* of the two acids and the phosphorus determined, using the porcelain dish. If the standard is found to run higher than it should, the deduction necessary to correct it constitutes the blank to be subtracted from the phosphorus found in the sample.

Any method with which the writer is acquainted, using a carbonate and niter fusion of materials containing tungsten for the purpose of obtaining the percentage of phosphorus therein, gives only a fourth, or less, of the actual content of the latter element. The following results are only a few of those obtained in this laboratory and are given in proof of the above statement:

COMPARISON OF FUSION AND EXTRACTION METHODS

Sample.	Percentage, Author's Extraction Method	Phosphorus Found by Fusion with $Na_2CO_3+KNO_3$
Ferro-tungsten No. 18	0.322 0.350 0.345 0.330	0.096 0.088
A high phosphorus pig iron (0.73 per cent P) 0.5 gram tungsten powder (98 per cent pure) per gram of iron ..	0.70	0.098 0.095
"Tungsten cake".	0.101 0.102	0.008
Tungsten powder oxidized to WO_3 at low red heat before extraction	0.113	0.007

Phosphorus in Tungsten Ores.—Here the procedure differs only in the manner by which decomposition is effected. Grind the ore to the finest possible state of division; extract at nearly boiling temperature with 100 c.c. conc. hydrochloric acid in a No. 5 porcelain dish. About every thirty minutes, add 0.1 gram additions of $KClO_3$; on each addition of chlorate stir the sample off the bottom of the dish with a glass rod. Continue the heating, addition of chlorate, and stirring until the tungsten ore has changed from a brown color to yellow in case of the dark ores; or from a light gray or brown to a very bright yellow in case of scheelite ore. Evaporate to dryness; cover; add 50 c.c. concentrated HCl; heat ten minutes to dissolve the iron and manganese; add 50 c.c. of water and heat fifteen minutes to allow the tungstic acid to separate well; cool and mix in some paper pulp. Filter through a double filter; wash with one part of hydrochloric acid diluted with twenty parts of water. Evaporate the filtrate and washings to 5 c.c. and add 75 c.c. of concentrated HNO_3; heat with the cover on the dish until all red fumes are gone and no further spraying occurs; remove the cover again and evaporate to 10 c.c.; add 50 c.c. of concentrated nitric and evaporate to 10 c.c. again; dilute with 15 c.c. of water and mix well. Filter into a 6 oz. beaker; wash with a 1 per cent by volume solution of nitric acid, fifteen or twenty times. Evaporate the filtrate and washings to 40 c.c. in the beaker; boil with a slight excess of permanganate solution. Add just enough ferrous sulphate to clear the excess of the hydrated oxide of manganese and boil again five minutes. Add 50 c.c. of molybdate solution to the hot fluid in the beaker and finish the analysis as in phosphorus in steel.

By careful heating and small additions of the chlorate, together with further applications of acid, if necessary, many dark ores can be so completely decomposed as to attain a clean orange color. The more complete the decomposition, the more perfect will be the extraction of the phosphorus. The hard black ferberites are the slowest to yield and take on the yellow color. The decomposition can be done to the best advantage at a low digesting heat and will require at least five or six hours.

This somewhat lengthy method is the only one that the author has found reliable, thus far, for technical purposes in tungsten ores. The latter may contain all the way from slight traces up to 0.500 per cent phosphorus. The fusion method with these ores gives just as low results as with the ferro-tungsten.

The cause of the low results is the formation of phospho-tungstic acid; this is carried from the solution with the main tungstic acid that forms when the sodium tungstate is decomposed by acidulation and evaporation with acid.

Phosphorus in Metallic Tungsten Powder, Tungstic Oxide and Tungstic Acid.—Ignite the tungsten powder at a red heat with frequent stirring until it is all converted to the yellow oxide. Then extract exactly as in tungsten ore for at least six hours and finish according to the ore method.

The original oxidation is best accomplished by weighing the sample into the dish in which the extraction is to be made and then placing dish and all in a muffle which is at a low red heat.

Tungstic acid and oxide do not require heating to redness. Their analysis for phosphorus is exactly like that for ores, beginning with the hydrochloric acid, chlorate treatment.

Reserve the tungsten residues that are filtered out after the extractions and evaporations for the tungsten determination. The purification of these residues will be described under Tungsten in ore, page 102.

NOTE.—It may be well in this article to caution those who have occasion to determine the phosphorus in molybdenum compounds, that any molybdic acid separating out of acid solutions containing phosphorus will carry a considerable amount of the latter element out, forming the analogous compound phospho-molybdic acid.

Method.—*The Determination of Tin in Metallic Tungsten Powder.*—Weigh 1 gram of finely ground sample into a porcelain boat of size $2\frac{3}{4}$ inches × $\frac{1}{2}$ inch. Spread this material out in as thin a layer as possible. Place this boat in the quartz tube of the same apparatus as is used for the determination of oxygen. Let the hydrogen pass at 950° C. or thereabouts for one hour. The hydrogen should pass through the furnace considerably faster than it does for oxygen determination. Turn off the current and continue to pass hydrogen until the furnace is cooled sufficiently, i.e., below a red heat, so that the hydrogen will not explode when the stopper is removed for withdrawal of the boat. All the contents of the boat should now have the gray color of metallic tungsten. Unless it has this color, it should be returned to the furnace and heated further as before. When the material is properly reduced, remove it to a small agate mortar; pulverize it, taking care not to lose any of the substance. Then transfer the finely ground tungsten powder to a 5-inch casserole; add 100 c.c. of concentrated hydrochloric acid; heat the dish for six hours in boiling water, with frequent small additions of potassium chlorate. Add about 1 gram of this salt every hour. Stir the material well off the bottom of the dish with each addition of the potassium chlorate. Add 100 c.c. of water; stir well ; filter; wash with dilute hydrochloric acid water; add 10 c.c. of cinchonine solution; dilute to 400 c.c. with water; stir thoroughly; let stand overnight; filter from any precipitate of tungsten cinchonate; wash with solution containing 5 c.c. of cinchonine solution, diluted with 500 c.c. of water; add ammonia to the solution of the sample until the iron precipitate, or other precipitates that may have formed, seems to dissolve rather slowly. Heat the perfectly clear solution to about 80° C.; pass H_2S slowly through it until the precipitate of tin sulphide separates out well. This will take several hours' passage of the gas. Filter. Wash with H_2S water. It will require about fifty to sixty washings to remove the iron. Burn the filter paper and sulphides of tin, copper, molybdenum, etc., at a red heat in an open porcelain crucible until the residue is of a grayish white; if copper is present there will be black spots in the ash. If tinged with red, iron is present. In either case warm the ash in the crucible with 10 c.c. of 1.20 nitric acid, covering the crucible with a small watch glass during the heating period, which should continue until any slight effervescence that may occur has ceased. If bismuth be present, it is quite noticeably reduced during the removal of the carbon of the filter paper. After heating for, at least, ten minutes, and longer if necessary, the watch glass is removed, rinsing off its under surface and allowing the washings to run into the crucible. Evaporate the contents of the crucible to dryness and gently ignite it until all nitrates are decomposed. Then weigh the residue, after igniting it at a red heat for thirty minutes to render the tin insoluble. This weight will be that of the oxides of Sn, Cu, Mo, Sb, Bi, and a little Fe. To remove the Cu, Fe, and Bi warm the ash in the crucible with 10 c.c. of 1 : 1 HCl, heating for ten minutes just below boiling; rinse the contents of the crucible onto a small filter; wash the same with 1 : 20 HCl and, finally, with some water. Ignite the paper in the same crucible again until white to grayish white at a low red heat. Moisten with conc. nitric acid and ignite again to oxidize any metal formed.

To remove molybdenum extract this residue with 5 or 10 c. c. of strong ammonia. Use ammonia that is freed from any sediment or floating particles, or scales of glass. Filter; wash paper with ammonia and put it back again into the same crucible, and burn the residue at a low heat. This residue will now consist of tin oxide plus a little silica. Weigh the residue; and remove it to a platinum crucible. Add four to five drops strong sulphuric acid, and then 10 c.c. c.p. hydrofluoric acid; evaporate as in the determination of tungsten. Drive off sulphuric acid; weigh the white to grayish white residue as oxide of tin. This weight multiplied by 0.7876 gives the equivalent weight of metallic tin, which is converted to percentage by the usual calculations.

In the presence of much tin and bismuth it is more accurate to proceed as given in the foregoing method until the sulphides of tin, etc., have been filtered and washed when, instead of igniting the same, the mixture of sulphides is placed, filter and all, in a porcelain casserole, covered with *yellow* ammonium sulphide and warmed on a water bath with frequent stirring for three hours. The pulp and solution are then filtered and washed with water containing 10 c.c. of the yellow ammonium sulphide diluted with 500 c.c. of water. After thorough washing the filtrate and washings are made slightly acid with HCl and saturated with H_2S when all of the tin will separate out; it is then filtered out; washed with H_2S water; ignited; treated with nitric acid; ignited again and weighed as tin oxide, now free of bismuth, all of the latter having been filtered out with the paper pulp, as sulphide, after the ammonium sulphide extraction.

If the amount of tin and bismuth in solution is large, for example 100 mgs. of tin and 50 mgs. of bismuth, it is advisable to again heat the precipitated sulphide of tin as before with the yellow ammonium sulphide, when the tin sulphide should be free of bismuth.

The combined filtrates from the two extractions of the tin sulphide are made slightly acid and the bismuth therein is precipitated with H_2S; washed with H_2S water; ignited at a low red heat in a porcelain crucible; the oxide of bismuth is heated with a mixture of a little conc. HNO_3 and conc. HCl until all black metallic residue is dissolved; it is then evaporated to dryness with an excess of nitric acid; ignited to the yellowish Bi_2O_3; and weighed as such and calculated to metal by use of the factor 0.89655.

For the separation of as much tin and bismuth as mentioned, use 140 c.c. of conc. ammonia saturated with H_2S for each extraction; and dissolve 1 gram of flowers of sulphur in this amount of ammonium sulphide before pouring the latter over the mixture of the sulphides.

again until white to grayish white at a low red heat. Moisten with conc. nitric acid and ignite again to oxidize any metal formed.

To remove molybdenum extract this residue with 5 or 10 c. c. of strong ammonia. Use ammonia that is freed from any sediment or floating particles, or scales of glass. Filter; wash paper with ammonia and put it back again into the same crucible, and burn the residue at a low heat. This residue will now consist of tin oxide plus a little silica. Weigh the residue; and remove it to a platinum crucible. Add four to five drops strong sulphuric acid, and then 10 c.c. c.p. hydrofluoric acid; evaporate as in the determination of tungsten. Drive off sulphuric acid; weigh the white to grayish white residue as oxide of tin. This weight multiplied by 0.7876 gives the equivalent weight of metallic tin, which is converted to percentage by the usual calculations.

In the presence of much tin and bismuth it is more accurate to proceed as given in the foregoing method until the sulphides of tin, etc., have been filtered and washed when, instead of igniting the same, the mixture of sulphides is placed, filter and all, in a porcelain casserole, covered with *yellow* ammonium sulphide and warmed on a water bath with frequent stirring for three hours. The pulp and solution are then filtered and washed with water containing 10 c.c. of the yellow ammonium sulphide diluted with 500 c.c. of water. After thorough washing the filtrate and washings are made slightly acid with HCl and saturated with H_2S when all of the tin will separate out; it is then filtered out; washed with H_2S water; ignited; treated with nitric acid; ignited again and weighed as tin oxide, now free of bismuth, all of the latter having been filtered out with the paper pulp, as sulphide, after the ammonium sulphide extraction.

If the amount of tin and bismuth in solution is large, for example 100 mgs. of tin and 50 mgs. of bismuth, it is advisable to again heat the precipitated sulphide of tin as before with the yellow ammonium sulphide, when the tin sulphide should be free of bismuth.

The combined filtrates from the two extractions of the tin sulphide are made slightly acid and the bismuth therein is precipitated with H_2S; washed with H_2S water; ignited at a low red heat in a porcelain crucible; the oxide of bismuth is heated of wheat flour, and secures an absolutely uniform sample. The smaller sample accumulated from the squares is well mixed and is in turn spread into a layer of one-eighth inch thickness and sampled again in squares to about 10 grams. The latter amount is then ground in an agate mortar.

RESULTS OBTAINED FROM THE TWO METHODS OF SAMPLING

	Five Pound Sample Ground in the Jar Mill		Ten Gram Sample Ground in the Agate Mortar	
	Per Cent WO_3	Per Cent SiO_2	Per Cent WO_3	Per Cent SiO_2
Portuguese wolframite	70.59	1.87	70.51	1.84
Australian wolframite	69.29	5.23	69.30	5.33
Wolframite from the "Straits"	66.00	2.38	65.96	2.34
Wolframite from the "Straits," Lot A	68.81	3.73	68.88	3.62
Portuguese wolframite . . .	70.70	2.04	70.79	2.15
"Straits" wolframite	70.37	2.04	70.46	2.04
Portuguese wolframite, car 560,151.	70.34	2.09	70.52	1.85
Wolframite from Randsburg, Cal	73.58	2.60	73.48	2.64
Straits wolframite, car 10,155 .	69.08	1.95	69.00	1.92
Canadian scheelite. . .	71.82	4.20	71.88	4.20
Portuguese wolframite, car 52,974.	70.48	1.87	70.4	. . .

	Six Pound Sample Ground in the Jar Mill		Ten Gram Sample Ground in the Agate Mortar	
	Per Cent WO_3	Per Cent SiO_2	Per Cent WO_3	Per Cent SiO_2
S. S. Patricia, car 58,714	66.00	5.73	66.00	5.72
California scheelite, car 26,140	69.23	7.47	69.10	7.49
Australian wolframite, car 534,453	69.6	2.33	69.5	2.40
Wolframite S. S. Cleveland, W-1	69.6	1.06	69.7	1.05

After making these tests extending over several months the author came to the following conclusions:

(1) The best grade of porcelain and of hand picked flint pebbles must be used.

(2) The jar must be filled with enough of the sample to prevent the pebbles from rubbing on each other or on the walls of

the jar, i.e., a jar calling for a maximum charge of 5 pounds, for example, must be used with that amount in it, otherwise notable amounts of silica will be gathered up during the grinding. On the other hand practically no silica is obtained and no appreciable lowering of the tungsten content was noted except in one instance car 11,611 was apparently lowered in tungsten content from 72.18 to 71.95.

(3) The proper amount of material to place in a jar of a given size in order to secure perfect grinding, without adding silica, should be determined by experiment.

(4) The advantages of this apparatus are that a large sample can be taken; that perfect grinding and perfect uniformity of sample are obtained; and that the grinding goes on leaving the operator free to attend to other work.

(5) The only disadvantage is the first cost, but in a large works where many shipments must be sampled, the saving of labor makes the cost insignificant.

Determination of Tungsten in Tungsten Ores

(2) The Determination of Tungsten in Ores without a Preliminary Fusion.—The writer has always refused to assay tungsten ores or other tungsten-bearing materials by precipitation as mercurous tungstate for the reason that any phosphorus, molybdenum, aluminum or vanadium present would be precipitated with the tungsten and counted as such. Tin also is a common constituent of tungsten ores. The writer has often encountered the presence of this element in shipments of wolframite ores from traces up to 10 per cent. The sodium carbonate fusion of the ore which is the usual preliminary to the mercurous nitrate precipitation contaminates the sodium tungstate with sodium stannate. In scheelite ores it is a common thing for the phosphorus to be as high as 0.150 per cent and sometimes as much as 0.500 per cent. Slimes and other low-grade concentrates are especially liable to be high in this element. The writer has had some residues very rich in tungsten running to 0.400 per cent. Alumina is a frequent constituent to be guarded against. Again, as is well known, it is extremely difficult to wash sodium salts out of tungstates precipitated from a solution of the former by mercurous nitrate.

After some years' experience in this line of analytical work, a method was evolved which is perfectly fair to both buyer and seller. It avoids the tedium of the sodium carbonate fusion of the main sample and all of the unpleasantness and inherent inaccuracies of the mercurous precipitation. After more than ten years almost daily use of this method the author again offers it in detail as giving the true tungsten.

Method.—The ore is ground to the finest flour either by hand in the agate mortar, or in the laboratory jar mill; after drying this powder for two hours at 105° C., one gram of it is weighed into a 4½-inch casserole of R. B. type with porcelain handle. 100 c.c. of conc. hydrochloric are poured on the ore; the dish is covered with a watch glass and heat is applied for one hour, keeping the acid below boiling; 200 mgs. of crystals of potassium chlorate are now quickly added, covering the casserole again. After the first violent action is over, the ore is carefully and completely stirred off the bottom of the casserole and the mild digesting heat is continued for another hour when the same amount of chlorate is again added and the sample is again stirred up and so on until about 2 grams of the chlorate have been consumed and the ore has been thoroughly decomposed as shown by its color having changed to bright yellow, or in some ores to an orange shade. Scheelite requires four hours of this treatment for decomposition; the dark ores, wolframite and ferberite, turn yellow in six hours. The watch glass is then removed and its under side is rinsed off with water, allowing the rinsings to run into the casserole, the contents of which are now evaporated to dryness on a graphite bath, consisting of a 6-inch pudding pan filled a little over half full with chip graphite. Each unit is heated by an ordinary Bunsen burner and requires but very little gas, a flame from 1 to 1½ inches in length being sufficient for all kinds of evaporations. The layer of graphite is from three-quarters to 1 inch thick. This enameled pan is mounted on a clay flame guard or support. If it is desired to raise the temperature of the dish to a dull red, the pan can be removed and the flame length increased. This combination is acid-proof to a practical extent; occasionally it becomes necessary to remove the Bunsen burner and pour a little 1 : 1 hydrochloric acid through the inlet tube to clear it out. After rinsing out the acid with water, it is ready for use again. The graphite is indestructible and the whole outfit is quite inexpensive and lasts a long time. Illustration No. 44 shows twenty-four of these units in use and No. 43 gives a closer view of a portion of a group. The outside depth of the pan is 1¾ inches.

After evaporating the decomposed ore to dryness, 30 c.c. of conc. hydrochloric acid are poured on it; heat is applied; 70 c.c. of water are added, followed by thirty minutes further warming, and some stirring. The crude tungstic acid and silica are filtered through a double 11 cm. ashless filter. Before performing the filtration, a three-quarter inch ball of ashless filter pulp is thoroughly mixed with the tungstic acid to hasten filtration and secure a perfect washing. The mixture on the filter should be washed with great care, giving it not less than sixty washings with 1 : 30 hydrochloric acid to insure removal of potassium salts. If the glass rod or the casserole shows yellow stains of tungstic acid, these can be removed by pouring over them a few drops of conc. ammonia. This solution is then rinsed with a thin jet of water into the filtrate and washings from whence it is recovered along with any metatungstates as follows: 50 c.c. of cinchonine solution are stirred into the filtrate and washings which are then allowed to stand for from 6 to 12 hours to permit the last traces of the tungsten to separate out. It may be of interest, in passing, to state that when determining sulphur in tungsten-bearing materials of any kind by the barium sulphate method, the author always first removes the last traces of tungsten that are almost certain to be present by means of 12 hours' standing with cinchonine added. It is easily seen that a few milligrams of tungstic acid contaminating the barium sulphate would cause a serious error. Cinchonine used for such work must be first washed free of sulphates before using it. This can be easily done by placing the crystals on a large filter paper and rinsing them with distilled water until the washings no longer give a cloudiness with barium chloride. Any tungsten-cinchonine precipitate must be washed with water containing some cinchonine solution as the precipitate is soluble, or runs through the filter if washed in the same manner as the tungstic acid.

The filter papers carrying the tungstic acid and that obtained by the cinchonine are dried in an air bath and then smoked off in a 20 c.c. platinum crucible. The heat is then raised to low redness only, and the heating is continued until the residue is yellow and free of carbon. This ash is cooled in a desiccator and weighed as WO_3 plus some Fe_2O_3, Al_2O_3, SnO_2, Mn_3O_4, CaO, Ta_2O_5, Nb_2O_5, MoO_3, CuO, and all of the SiO_2. For extreme accuracy in silica, the filtrate and washings from the tungstic acid should be evaporated again to dryness before adding the cinchonine; the residue dissolved as before in hydrochloric acid and water; any small insoluble residue of WO_3 plus SiO_2 so obtained is filtered out; washed; burned with the principal precipitate and then the cinchonine solution is added to this final filtrate and washings to get the final traces of dissolved metatungstates.

The weighed residue consisting of total WO_3 plus SiO_2 plus the other oxides mentioned is now evaporated with from five to ten drops of conc. sulphuric acid together with 15 c.c. of c.p. hydrofluoric acid in a muffle furnace lined with ¼ inch asbestos board to prevent bits of brick from dropping in the work. The writer uses for these evaporations a small reverberatory furnace. The gas flame is not allowed to come above the bridge wall. By heating in this manner there is never any danger of loss of analyses by spattering. (See page 438.)

The crucible is left in this drying furnace until the heavy white fumes of sulphuric anhydride are no longer given off. The crucible is raised to a dull red heat on a Chaddock burner and then cooled in a desiccator and weighed again. The difference between this weight and the weight of the WO_3, etc., should equal the silica present in the ore. But if the per cent so found should exceed 8 per cent SiO_2, then it is safer to repeat this evaporation to insure the complete removal of the silica. The author has found that this second evaporation, with additional sulphuric and hydrofluoric acids, should in no case be omitted when the silica content reaches from 30 to 60 per cent as it often does in unconcentrated ores and slimes. Titanic oxide is frequently present with the WO_3, etc., and for this reason the sulphuric acid should always be added in at least the quantity specified to prevent its volatilization as fluoride.

After weighing the now silica-free WO_3, etc., it is fused at a bright red heat with twenty times its weight of anhydrous sodium carbonate. It is kept molten for twenty minutes. The melt is dissolved in hot water in a 100 c.c. platinum dish, or if no platinum is available, then the fusion can be leached in a porcelain vessel; do not boil, but warm gently, as otherwise the porcelain will be attacked and the accuracy of the analysis will be impaired.

If the water solution of the sodium carbonate fusion of the silica-free WO_3 has a greenish tint due to the formation of sodium manganate, a few drops of alcohol are added and the solution is warmed until this color disappears, the manganese completely precipitating as hydrated oxide. A little paper pulp is added; the various oxides are filtered out; washed repeatedly to entirely remove the sodium salts; ignited at a red heat to remove the carbon. If the residue in the crucible sinters on ignition it is imperfectly washed and contains sodium salts, and a repetition of the fusion, solution and washing is necessary. It is safer to fuse the ignited oxides again in any case if their total weight exceeds 4 or 5 mgs., as part of this weight is almost certain to be WO_3. After the second fusion, solution, washing, and ignition, the oxides are weighed and their amount is deducted from the weight of WO_3 obtained after expelling the silica. The remainder represents the total WO_3 plus any aluminum, tin, bismuth, molybdenum, copper, tantalum, and niobium that may have gone into solution as sodium compounds. To correct for all but the molybdenum and copper, the two sets of filtrates obtained from the two fusions of the total oxides of WO_3, etc. (silica-free), with 20 grams of sodium carbonate, are made just acid with HCl; then just ammoniacal; add 10 c.c. excess of NH_4OH; heat to boiling; remove from fire. Add HCl (1 : 1) until solution is just faintly alkaline. Any Al, Ta, Nb, Sn that have gone into the solution in combination with the sodium carbonate and would be otherwise counted as WO_3 will now be precipitated. Filter off the flocculent precipitate if any (and there nearly always is some); wash same eighty times with H_2O plus NH_4NO_3; combine this filter with the doubly fused water insoluble, ignited oxides of iron, etc., already mentioned, that should be held for this purpose; burn all in a platinum crucible at the lowest heat to a constant weight; heat to a fairly bright red toward the end; deduct the weight from that of the crude WO_3, after the silica has been removed from it in the manner already described. This weight will constitute the total pure WO_3 except that carried down by the NH_4OH precipitate just described.

To obtain this tungsten, fuse this precipitate of Al, Ta, Nb, Sn, after weighing it, with Na_2CO_3 in the platinum crucible; leach out the fusion with water; make it acid with some excess of HCl; heat if necessary; add cinchonine to the clear, or perhaps slightly clouded solution; any tungsten in the solution will separate out in a few hours. Filter; wash with cinchonine wash; ignite and weigh it and add the weight of it to the pure tungsten content already found obtaining weight A.

A further correction must be applied to the tungstic acid content A for any Mo or Cu that have gone into the solution of the leached carbonate fusion. To make this correction, the ammoniacal filtrate from the Al, Ta, Nb, and Sn, etc., is treated with 4 grams of tartaric acid to hold back the WO_3. It is then made faintly acid with HCl and saturated with H_2S for one hour; filter off any sulphides that are found here; wash sixty times with H_2S wash, containing two or three drops of HCl; burn at the lowest possible heat that will remove the paper, in a weighed porcelain crucible. Weigh the ash; extract it with HCl (1 : 1) for one hour; filter; wash with HCl wash (1 : 20); burn the insoluble in the same crucible; weigh the ash and the difference in weight between the first ash and the second ash equals the Mo or Cu content that has been counted as tungsten; subtract this weight from the total pure tungsten content just previously noted (A). This final corrected weight should now constitute the total tungsten, free from all impurities and be calculated to percentage content of the ore.

However, there is still a further chance for error. The sodium carbonate used may contain enough iron to increase the deduction made when the WO_3, etc., is fused twice to correct for any iron remaining in it after the removal of the silica with HF. Therefore blanks for iron should be run on the carbonate and the final WO_3 should have an additive correction made to it equal to the amount of the Fe_2O_3 found in as much of the same sodium carbonate as was used in the last two fusions. This correction will frequently increase the WO_3 content in the final weight to the extent of 0.2 to 0.3 per cent content of WO_3. In a 30-ton lot of ore this means considerable in money value.

This method is applicable to ferberite, wolframite, huebnerite, scheelite, cupro-scheelite, lead-tungsten ores, arsenical-tungsten ores and tin-tungsten ores. Such ores are on the market and have been for many years that are liable to contain these impurities. The latter all more or less seriously affect the determination of the total exact WO_3. The impurities are present in the following percentage ranges based on the analysis of ores from all parts of the world; China, Japan, South America, Australia, Spain, the United States, and Mexico.

The following shows about the percentage range of these impurities:

Arsenic	from traces to 3 5 per cent
Lead	from traces to 8 0 per cent oxide
Tin	from traces to 15 0 per cent oxide
Copper	from traces to 3½ 4 per cent oxide
Bismuth	from traces to 2 0
Phosphorus	from traces to 0 5

THE DETERMINATION OF LEAD, ARSENIC, BISMUTH, COPPER, ANTIMONY, TANTALUM WITH NIOBIUM, MOLYBDENUM, AND SULPHUR IN TUNGSTEN ORES

Lead.—Digest 2 grams of the finely ground ore in a 500 c.c. cone flask with a mixture of 30 c.c. conc. nitric acid and 70 c.c. conc. hydrochloric acid, for several hours on a graphite bath (see page 100) until the ore is yellow or greenish yellow and all brown fumes are gone, adding more of the mixed acids if necessary.

When no further increase in the yellow color can be detected, the contents of the digesting flask are diluted with a mixture of two parts of conc. HCl and one part of H_2O. This strength of acid is used to prevent the precipitation of some of the lead, along with the tungstic acid in the form of chloride. The oxides of tungsten, silicon, etc., are filtered out and washed on the filter with one part of conc. HCl diluted with twenty parts of water. Give the residue on the filter about fifty washings.

Add to the filtrate and washings a slight excess of ammonia; then acetic acid in excess or about 80 c.c. of the glacial acetic acid in all. Pass H_2S through the hot acetic solution until any precipitate that may form is collected and settles well, when the H_2S is shut off. Filter off the sulphides, which will contain all of the lead, copper, and bismuth, some of the tin and considerable iron sulphide. Wash the mixed sulphides with H_2S water containing two drops of conc. HCl in 500 c.c. of water, using a cold wash.

Burn the thoroughly washed precipitate in a porcelain crucible by smoking off, raising the heat to low redness only after the paper is entirely charred; moisten the ash when all of the char has been burned out with a few drops of conc. nitric acid to dissolve any metallic globules or fine gray particles of metallic lead or bismuth that may have been reduced from the burning of the filter paper. Dry cautiously to remove the excess of acid and then again ignite at the lowest red heat. Put the crucible and all in a casserole with 100 c.c. of conc. HCl; heat until all is dissolved but a little silica from the paper or tin oxide.

Remove the crucible; rinse off the side of the crucible, letting the washings run into the solution from which it was taken. Add to this HCl solution 50 c.c. of 1 : 3 H_2SO_4 and evaporate to thick white fumes of sulphuric anhydride; cool; add 100 c.c. of water; heat until all but the lead sulphate is dissolved; add 50 c.c. more of the 1 : 3 H_2SO_4 and again take to thick fumes; cool; add 150 c.c. of water; heat as before until all but the lead sulphate is in solution; then add 50 c.c. of 95 per cent alcohol and let the lead sulphate settle overnight. Filter off the crude lead sulphate; wash it with cold water containing 5 c.c. of conc. H_2SO_4 per 500 c.c., giving it about forty washings.

The filtrate from the crude lead sulphate is made slightly ammoniacal and then slightly acid with HCl and saturated hot with H_2S to precipitate the main Cu and bismuth. The bismuth and copper sulphides are thoroughly washed with H_2S water; dried in a porcelain crucible; the paper is smoked off; the heat is then raised to low red to remove all of the carbon of the filter paper; the ash in the crucible, which should be yellowish white, especially when hot, is mainly Bi_2O_3, and some metallic bismuth. It is evaporated several times to dryness with a few drops of nitric acid to convert all of the bismuth to oxide. This oxide will be blackened if considerable copper is in the ore or metal. If much bismuth and copper are present some of these elements will cling to the crude lead sulphate obtained in the manner just described under *Lead.* The lead sulphate is purified from any Bi or Cu still with it by dissolving it in 100 c.c. of conc. HCl. To this solution 50 c.c. of 1 : 3 sulphuric acid are added and all is evaporated to thick white fumes of sulphuric anhydride; cool; add 50 c.c. of water and 50 c.c. more of the dilute sulphuric acid and again take to thick fumes; heat with water until all but the lead sulphate is dissolved; add alcohol; let stand overnight. The lead sulphate is filtered out; washed with sulphuric acid water; smoked off in a porcelain crucible; heated at a low red until the residue is white; it is evaporated with a few drops of nitric acid to convert any metallic lead to oxide. The sulphate and oxide mixture is evaporated with a few drops of conc. sulphuric acid to convert the oxide to sulphate. The now pure lead sulphate is weighed and calculated to metallic lead by the factor 0.6832 if obtained from metallic tungsten. If obtained from ore it can be calculated to oxide by multiplying the sulphate obtained by the factor 0.7360.

The filtrate and washings from the pure lead sulphate contain the remainder of the copper and bismuth. This filtrate is made slightly ammoniacal and then slightly acetic. The copper and bismuth, if there be any in this filtrate, are then recovered by H_2S, as in the main copper and bismuth; filtered out; washed; ignited; and combined with the main copper and bismuth obtained as already described. The total copper and bismuth can be weighed as oxides; dissolved in HCl. The copper can then be determined by the cyanide titration; calculated to copper monoxide and deducted from the weight of the total oxides of copper and bismuth. The remainder is calculated to per cent as Bi_2O_3 in the case of ore, or in the case of metal to metallic bismuth by the factor 0.8965.

ANALYSES OF SOME ORES SHOWING RANGE OF ARSENIC, COPPER, LEAD, AND BISMUTH THAT ARE LIABLE TO BE ENCOUNTERED IN TUNGSTEN ORES

Tungsten oxide	54.20	66.80	54.90	61.05	60.00	50.00
SiO_2	10.80	7.59	4.18	2.68	4.00	7.00
SnO_2	1.02	0.61	2.20	0.20	1.40	18.56
Bi_2O_3 .	1.38	0.10	3.55	0.20	5.28	0.35
CuO . . .	0.70	1.70	0.30		0.06	. . .
PbO	4.86	0.01	11.49		0.63	0.007
As.		0.04	1.02	3.49	0.51	0.67
Mn.	.	0.01	3.38	0.78	7.69	1.77

RESULTS OBTAINED ON KNOWN MIXTURES

LEAD ADDED TO A TUNGSTEN ORE		BISMUTH ADDED TO A TUNGSTEN ORE	
Added Lead, Gram	Found Lead, Gram	Bismuth Added, Gram	Found, Gram
0.050	0.048	0.050	0.052
0.025	0.025		

Arsenic in Tungsten Ores and Metals.—The following rather tedious method is the only one that the author can recommend to obtain the *total* arsenic in tungsten ores Results by any form of distillation method were not at all satisfactory. The weighing of the arsenic as phosphate the writer has found to be full of sources of error, the tendency being at all times to get results that are too low. The distillation method also gave low results. The writer bases his method on Bunsen's scheme of weighing the pentasulphide of arsenic. He has found the following method adapted to all arsenic determinations from traces to the highest percentages, using it to determine the arsenic content of mispickel, for example.

It should be stated that only certain kinds of asbestos can be used for the weighing pad, as some kinds seem to lose weight indefinitely, no matter how much they are washed. The analyses given on page 110 show the kind of asbestos that can be depended upon to give constant, i.e., undiminishing weight after it has been once thoroughly washed. The other type keeps dissolving away indefinitely.

ARSENIC

Five grams of the pulverized ore or metal are extracted in a 300 c.c. casserole with a mixture of 100 c.c. of conc. nitric acid and 100 c.c. of conc. hydrochloric acid. The digestion is continued until the sample is yellow to greenish yellow. This extraction should continue for several hours. Then evaporate low; add 100 c.c. of conc. HCl and take low again but not to dryness. During the evaporations add a few crystals of potassium or sodiun chlorate at intervals of every half hour. Then remove *entirely* the excess of chlorate and chlorine by taking low once more with 100 c.c. of HCl. Filter out the tungsten and silica and wash the same with dilute HCl wash water. Add 100 c.c. of HCl to the filtrate and washings and again evaporate low to insure that all of the free chlorine is perfectly removed. If the concentrated solution is not perfectly clear on diluting it with water it should be filtered and the filtrate and washings must be evaporated to about 10 or 15 c.c. Now add 100 c.c. of HCl and enough water so that the solution contains two parts of conc. HCl to one part of water. The beaker containing this 2 : 1 acid solution is then placed in cold water until cold. This strong acid and cold solution is to insure the precipitation of the arsenic as the pentasulphide. The strong acid will also prevent the co-precipitation of any bismuth, lead, tin, and molybdenum that may be present in small amounts. Pass H_2S through this solution for three hours. Then let it stand overnight to insure the complete precipitation of the arsenic. This long standing is very necessary, especially if the per cent of arsenic is very low. The mixture of arsenic pentasulphide, sulphur, and copper sulphide (if any be present) are filtered out and washed with one part of conc. HCl diluted with twenty parts of water, saturated with H_2S. This will require fifty washings, at least. Then wash with cold water to remove the acid. Put filter and all in a 100 c.c. beaker and beat it to a fine pulp with a glass rod. Then add to this pulp a mixture of twenty parts of hydrogen peroxide solution and twenty parts of conc. ammonia; stir well and let stand overnight; filter out the pulp, which should be now no longer colored yellow with arsenic sulphide; wash the pulp with water; neutralize the filtrate and washings with HCl, and then add to the neutralized filtrate twice its volume of conc. HCl and pass H_2S through this strongly acid solution until the arsenic separates out as the pentasulphide, which will now be free from sulphur. Let stand overnight again, as the pentasulphide separates very slowly in the strongly acid solution. The arsenic sulphide is now filtered on a washed, dried, and weighed long-fiber felt filter, using a porcelain Gooch crucible. This filter is dried and weighed at 100° to 104° C. to a constant weight. It is important to test the dried and weighed felt by pouring through it some 2 : 1 HCl. Wash out the acid with water; dry and weigh the crucible again at 105° C. The system should have the same weight as before within a half milligram. Some asbestos is worthless for this purpose, as it loses weight indefinitely, no matter how much it is washed before it is used for a weighing pad. The following analyses were made in this laboratory, one being of a long-fiber washed asbestos that was satisfactory and the other one was from an asbestos that continually lost weight, no matter how much it was boiled with aqua regia (twenty-four hours).

	Asbestos O K for Weighing Pads Washed Per Cent	Asbestos that Continually Lost Weight when Washed with Acid Per Cent
Silica	57 59	40 08
Iron oxide . .	2 77	3 64
Alumina . .	0 59	0 75
Lime	13 89	None
Magnesia . .	23 29	41 11
Ignition	0 84	14 22

Blanks should be run on the entire operations and the arsenic found, if any, deducted. A good way, and indeed the best way, to run a blank is to add to a tungsten ore that contains but a small per cent of arsenic (less than 0.05 per cent As) a larger known amount of arsenic, either as metallic arsenic or the natural sulphide, mispickel, is an excellent source of arsenic. The complete analysis of the mineral (get a pure sample from a firm that has a reputation for making a specialty of pure mineral specimens) can be made as a check on the arsenic determination that one makes by the foregoing method. The following is the analysis of a sample that the author used:

Arsenic.	45.25 per cent
Sulphur	20.00 per cent
Iron.	35.00 per cent

A weighed amount of this mispickel can be added to the ore to be analyzed and then put through all of the operations.

From the arsenic found, deduct the arsenic found by the same method in the same sample to which *no* arsenic has been added. Now if there be more arsenic found than was added to the ore, even after making the deduction just mentioned, then this excess, if any, will constitute the true blank to be deducted from all of the arsenic determinations made at that time and with the *same lot of acids or other chemicals.*

If much copper or molybdenum or both are present in the ore, then the As_2S_5 precipitate instead of being of a pure lemon yellow will be a dirty yellow or brownish, or blackish. In such event the arsenic sulphide, etc., should be again dissolved in the mixture of hydrogen peroxide and ammonium (conc.) neutralized, the excess of HCl added and the arsenic again precipitated with H_2S, saturating the solution in the cold for several hours and so on until the precipitate is obtained of a clear yellow color, when it will be fit to weigh as the pure pentasulphide of arsenic. If several per cents of copper or molybdenum or both are present, a much better way to get a pure yellow arsenic pentasulphide is to take the filtrate and washings from the last traces of the tungsten after all of the chlorine has all been removed as already described, and precipitate it with ammonia. There is generally enough iron present to carry out all of the arsenic and antimony. This precipitate, which should be red and contain fifteen to twenty times as much iron present as the total amount of arsenic and antimony present in the sample being tested, is dissolved off the filter with hot 1 : 1 HCl; the filter thoroughly washed. The solution and washings will contain all of the arsenic and antimony. It is evaporated to a definite volume; twice this volume of conc. HCl is added; the *cold* solution is saturated with H_2S; allowed to stand overnight when the arsenic pentasulphide is ready to be filtered off; washed with 1 : 1 HCl; then free of acid with cold water; filter and all beaten to a pulp; this mixture of paper pulp, free sulphur, and arsenic pentasulphide is treated with a mixture of twenty parts of hydrogen peroxide and twenty parts of conc. ammonia; stirred well. Filter out the pulp, which should be no longer colored yellow with arsenic pentasulphide; wash the pulp thoroughly; finish the filtrate and washings for arsenic as already described from this point on, weighing the arsenic as As_2S_5 which contains 48.326 per cent of As.

MOLYBDENUM, IRON, MANGANESE, LIME AND MAGNESIA IN TUNGSTEN ORES

The *molybdenum* is determined by fusion in the same manner as described for Mo in metallic tungsten on page 78.

Iron.—The iron will be mainly in the two filtrates obtained from the two evaporations to dryness to obtain the crude WO_3, etc. The remainder will be with the crude WO_3, etc. The latter, as has already been described, after being freed from silica (see page 72) is fused at a bright red with twenty times its weight of anhydrous sodium carbonate; dissolved in water; filtered out; washed; weighed; and fused, etc., again. The final double fused and weighed ash of iron, etc., will contain all of the iron, lime, magnesia, and manganese that escaped decomposition during the extractions with HCl and chlorate. This is then brushed out into a beaker; the crucible cleaned by warming in it some HCl; the residue in the beaker is dissolved also with HCl. The cleanings and the solution in the beaker are combined and evaporated low; and filtered into the two main filtrates from the two evaporations to dryness to obtain the first crude WO_3. The whole combination will now contain the entire iron, manganese, lime, and magnesia, and perhaps a milligram or two of tungsten in solution.

A double basic acetate precipitation can now be made as described on pages 244-245. The iron obtained from the second basic acetate precipitation will be free of manganese, lime, and magnesia; it can be ignited; dissolved in conc. HCl; evaporated low; water added; heated; filtered; evaporated to fumes with 30 c.c. of 1 : 3 H_2SO_4; taken up with water and 10 c.c. more of sulphuric acid and finished for iron by passing it through the reductor, in the manner described on page 366.

Manganese, Lime, and Magnesia.—The combined filtrates from the two basic acetate precipitations of the iron are evaporated low. Do not add any acid during this evaporation. If any small amount of red flakes separate out or the solution is yellowish, a little iron has gone into solution with the manganese, etc. Add a faint excess of ammonia. Do not heat, but filter out the small precipitate of iron; wash it thoroughly with water; dissolve it in a little HCl; wash the filter thoroughly; make a small basic separation of the iron; filter it out; wash it with acetate water; combine the filtrate and washings with that obtained when the small amount of iron hydroxide gotten with ammonia as just described was filtered out and washed. This total of filtrates will contain all of the manganese, lime, and magnesia, and can be analyzed in the usual way for these elements, as described on page 69, beginning at the place where the statement is made concerning basic slag that "The combined filtrates from the two basic acetate separations contain all the Ca, Mg, and Mn in the slag," under the heading, "*Oxides of Mn, Mg, and Ca.*"

The small amount of iron that may be found on evaporating the main basic acetate filtrates and washings to dryness should be added to the main iron just before evaporating it to fumes of SO_3.

Tin in Tungsten Ores.—This element is determined in the same way as described for tin in metallic tungsten powder. (See pages 93 and 94.)

Sulphur.—Sulphur can be determined by the same methods as given for metallic tungsten powder or ferro-tungsten. (See pages 76 and 77.)

CHAPTER IV

PART III

TUNGSTEN, SULPHUR, SILICON, MANGANESE AND PHOSPHORUS IN TUNGSTEN STEEL AND CHROME TUNGSTEN STEEL

First Method for Tungsten in Steel.—If the sample contains considerable chromium and tungsten, proceed as follows: Weigh from 1½ to 2 grams of drillings (see pages 130–131) into a No. 5 porcelain evaporating dish. Add slowly to the drillings, keeping the dish covered with a watch glass, a mixture of 30 c.c. conc. hydrochloric acid (1.20 sp. gr.) and 30 c.c. conc. nitric acid. Mix the two acids thoroughly before applying them to the steel if phosphorus is wanted. Heat until action ceases, and if the residue in the bottom of the dish is not bright yellow, repeat the addition of acid and continue to heat the dish until the tungsten residue is a clean yellow. Then remove the cover and evaporate the contents of the No. 5 dish to 15 c.c. Keep the heat low enough to prevent spattering. Do the evaporating on a graphite or sand bath. A 6-inch * pudding pan filled two-thirds full of graphite heated by an ordinary Bunsen burner makes a simple contrivance for the evaporations. The pan can be set on a tripod or an earthenware flame guard with the burner directly under the center of the pan. With such an arrangement, a flame an inch long will furnish sufficient heat. The guard answers the twofold purpose of supporting the pan and shielding the flame from currents of air. The earthenware has the additional advantage of being acid-proof. Add 50 c.c. conc. nitric acid. Put the watch glass on the dish and heat until action ceases. Remove the cover and evaporate to 15 c.c. Again add 50 c.c. conc. nitric acid and evaporate to hard dryness. Ignite the dish and its contents to a dull red, raising the heat *slowly* to prevent cracking. Set the dish over a bare flame for this purpose. The terra cotta flame guard, with the pan removed, answers quite well for a support during the ignition. Lower the flame slowly and set the dish on a warm place, cooling it gradually.*

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* See photo 43, page 488.

When the dish is just warm, pour into it 50 c.c. of conc. hydrochloric acid. Put the cover on and heat to slow boiling. Continue to boil until the residue in the bottom of the dish is bright yellow. Then remove the lid and evaporate to 15 c.c. Cool, and add 30 c.c. distilled water and ashless paper pulp. Filter on a double 11 cm. ashless filter (a double filter will run faster than a single one); wash with 1 : 20 hydrochloric acid until the washings give no test for iron with potassium or ammonium sulphocyanate. Return the filtrate and washings to the No. 5 dish for concentration.

Silicon.—Roast the paper out of the residue of tungstic and silicic acids in a weighed 20 c.c. platinum crucible. Do not heat tungstic acid to a bright red, as it slowly sublimes at high temperature. When the ash is bright yellow, free from black, cool in a desiccator and weigh. This weight will consist of mainly tungstic acid and silica contaminated with a small quantity of oxides of iron, and chromium, also, if the latter element be present. Add three drops of 1 : 3 sulphuric acid to the residue, and fill the crucible two-thirds full with c.p. hydrofluoric acid. Evaporate in a good draught to moist dryness. Drive off the sulphuric acid by heating the crucible near the top. When all heavy fumes are gone, heat to low red and weigh as $WO_3+Fe_2O_3+Cr_2O_3$. The difference between this weight and the first weight is the silica which has been volatilized. This loss of weight multiplied by 46.93 and divided by the weight of sample taken, equals the per cent silicon present in the steel. In the meantime the filtrate and washings from the first filtration should be evaporating until a slight ring of basic iron forms on the dish around the margin of the fluid. This ring dissolves rather slowly when the dish is rocked backwards and forwards. In other words, leave only enough acid to keep the iron in solution. (However, care must be taken not to overdo the removal of the excess of acid, as basic iron may separate in the solution when it is heated for the precipitation of phosphorus.) Add 20 c.c. of water; filter through a 9 cm. ashless filter into a 150 c.c. beaker. Wash the residue on the filter until all yellow color due to chloride of iron is gone. About fifteen washings should suffice. Wash every other time with 1 : 20 hydrochloric acid. If the volume of the filtrate and washings is over 50 c.c. reduce to that amount by evaporation. The filter at this point may be tinged slightly yellow with tungstic acid. It should be saved in that case and burned off with the main tungsten residue. The filtrate and washings, especially in very low percentages, i.e., when only a few tenths of a per cent of tungsten are present, are liable to contain tungsten in solution even after all of the foregoing operations. To guard against this it is safer to divide this filtrate and washings into two equal parts. Finish one part for phosphorus, multiplying the result by two before calculating to percentage. The other half of the filtrate and washings can be treated with cinchonine solution to make sure of getting all of the tungsten. This part should be allowed to stand several hours to permit any tungsten present to separate out. It is then filtered out; washed with cinchonine wash, 9 per cent (5 c.c. of cinchonine solution in 500 c.c. of water), ignited and weighed and twice its weight added to the main tungsten oxide weight before calculating it to percentage of metallic tungsten. For the determination of tungsten in the presence of molybdenum (see pages 156-158.)

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*It is much better to perform this ignition at a dull red heat, in an electric muffle. This prevents cracking of dishes and insures even heating.

Phosphorus.—The other half of the divided filtrate is finished for phosphorus by evaporating it to 15 c.c. with 50 c.c. of conc. nitric acid. Do this twice. Finish for phosphorus as in vanadium steels. See pages 41-44.

Tungsten.—The total residue in the crucible remaining after the removal of the silicon with HF and a few drops of H_2SO_4 ignition and weighing, constitutes the tungsten oxide plus small quantities of iron and chromium oxides is weighed again. If the original tungstic acid was thoroughly clean and yellow before the first evaporation to 15 c.c., then the amount of chromium oxide is negligible.

The $WO_3+Fe_2O_3+Cr_2O_3$ residue is fused with 5 grams of carbonate of soda. The melt is dissolved with hot water. The small residue of iron is filtered out and washed free of carbonate. It is burned to a red flake in the same crucible, which meanwhile has been thoroughly rinsed free of carbonate with distilled water. The residue is weighed and its weight deducted from the weight of the $WO_3+Fe_2O_3+Cr_2O_3$.

If the filtrate from the carbonate fusion is quite yellow, make it acid with sulphuric acid, boil with a slight excess of permanganate, and determine the chromium as in steels.* Calculate the milligrams of chromium found to chromic oxide, and deduct it from the $WO_3+Cr_2O_3$. The remainder is the tungsten oxide, which multiplied by 79.31 and divided by the weight taken for analysis gives the percentage of tungsten If the filtrate from the sodium carbonate fusion is only slightly yellow, the chromium may be ignored in the calculations.

(A) A good way to remove oxides of silicon, iron † and chromium from the tungstic oxide is to fuse with 5 grams of potassium bisulphate. This fusion can be made quickly. Heat the crucible at first to a very low heat, below redness, until the bisulphate is molten and slight fumes of sulphuric anhydride appear. Then raise the heat carefully to low redness. Keep the lid on the crucible, raising it only slightly to observe the progress of the fusion. When redness has been reached and all danger of spattering is over, raise the lid, and if the contents of the crucible are in a state of transparent fusion, with no yellow specks left undissolved, the fusion is completed. One can see the bottom of the crucible through the transparent molten mass, and, if only pure white flakes of silicic acid are floating about, the melt is perfect. Cool. Dissolve in 10 grams of ammonium carbonate and 100 c.c. of water, placing the crucible in the ammonium carbonate solution contained in a small casserole. Warm the casserole slightly to hasten matters. Keep it covered with a watch glass to prevent loss during heating. (Use a casserole if a platinum dish cannot be had.) Filter, adding a little paper pulp. Wash with water containing ammonium carbonate until the washings are no longer milky when acidulated with a few drops of hydrochloric acid and tested with barium chloride. Then wash ten times more. Ignite and weigh in the same crucible, and deduct the residue, which consists of all of the SiO_2, Cr_2O_3, and Fe_2O_3, from the WO_3, etc., and calculate to percentage. The residue of SiO_2, if not pure white, is evaporated with hydrofluoric and sulphuric acid in the usual way, and the loss of weight constitutes the silicon present in the steel when multiplied by 46.93 and divided by the weight taken for analysis.

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* Or determine the chromium by color, page 11.

† See bottom of page 104 relative to iron in sodium carbonate used to make the fusion for the removal of the iron.

The *sulphur* in such steels can be obtained by fusing 2 grams of thin drillings with 20 grams of sodium carbonate and 5 grams of potassium nitrate. Dissolve in water, filter, wash, roast, fuse again, acidulate with HCl, evaporate combined filtrates to dryness twice, filter after each evaporation, washing with 1 : 20 HCl; add cinchonine solution, filter after two hours; precipitate the filtrate with barium chloride and finish as in gravimetric sulphur in steels. Make blank determination on like amount of the flux and acids, proceeding exactly as in actual analysis, and deduct the sulphur found from that found in the fusion of the steel. Multiply the weight of barium sulphate less that found in the blank by 13.73, and divide by the weight of sample taken for analysis to obtain the per cent of sulphur.

Manganese.—Proceed as for manganese in steel when chromium is *present*, digesting the sample thoroughly with the mixture of acids as given. (See pages 32-33.)

The Ignition of Evaporating-dishes at a Dull Red Heat in the Determination of Silicon and Tungsten in Steels, Using an Electric Muffle Furnace

By far the best way to perform these ignitions, at a low red heat, is to use an electric muffle furnace. In this way the dish is heated uniformly and gradually all over. Also several ignitions can be carried out at the same time. By putting a fireproof mark on each dish and carefully wiping all dust, etc., from the surfaces of the different dishes, the latter can be put in the muffle in nest style. Dishes heated in a muffle are seldom cracked. In November, 1915, the writer published the following type of electric muffle for this and other ignition purposes, and a portable rheostat to control its temperature obtaining any heat from below redness to 1000° C. (See pages 119-121.)

A New Type of Portable Laboratory Rheostat.—Photo No. 3 shows the rheostat designed by the author with a view to making repairs more easy and to have a piece of apparatus with sufficient capacity to fill the needs of most laboratories. It consists of twenty-one coils of nichrome wire giving a total resistance of 30 ohms and a maximum capacity of 14 amperes. It can be used either on the furnace shown in Photo No. 3, at 16, or with

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* Read pages 121-122 on sulphur in chrome-tungsten-vanadium steels.

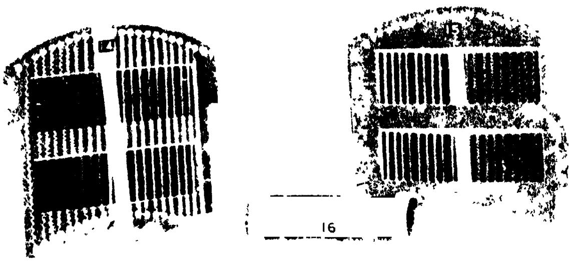


Photo No. 3.

Photo No 4.

the large one given in Photo No. 4. It holds the large furnace in Photo No. 4 for any length of time at any temperature from 200° C. up to 1000° C.

The rheostat occupies but a few inches of table width and can be set behind the other apparatus. Repairs are easily made and the white board of hard asbestos board gives a cheerful effect. If desired, two such rheostats can be bolted together, making a double instrument. The rheostat is practically indestructible so long as its capacity is not exceeded, as there is nothing about its design to get out of repair. In Photo No. 3, 15 is the front and 14 the back view showing details of construction.

A New Rectangular Laboratory Electric Muffle Furnace with Solid Heat Insulation Case.—The furnace shown in Photo No. 4 is in principle just the same as the cylindrical furnace described in Photo No. 3, No. 16. A white solid case of kieselguhr surrounds the heating element and working muffle which has an available working space of 11½×5×7 inches. This is ample for most laboratories. To control the temperature of the furnace the rheostat shown in Photo No. 3 is used and by means of it any desired temperature can be maintained for hours at a time up to 1000° C. The author keeps three furnaces of this size in constant service.

On account of the simplicity of construction, the repairs can be easily made and, as no insulating powder is used, the furnace is free from powder falling out into the working chamber. With the absence of the heat insulating powder the repairs are much simplified. The whole furnace is supported and enclosed in a stout, soft steel frame, which makes it very rigid.

The white casing makes an attractive looking piece of apparatus. The interior muffle on which the wire is wound is of a special composition which is now being tested out. This same composition used in combustion boats made the remarkable run of 525 steel combustions per boat with the test boats still in commission but considerably worse for wear. It is highly probably that the muffle will be equally superior to the old mixture for cylindrical core muffles.

The scheme is to keep these working muffles already prepared with the heating wire cemented on them ready for use so that repairs can be quickly made. As the furnace consists of but three parts its construction is considerably cheaper than that of the old types, besides having the advantages already mentioned. A slow stream of air from the compressed-air line is passed through the furnace during ignition of silicons or graphites.

The door opens horizontally: the author has found this arrangement to be much more desirable than the vertically opening door used in some of the old types.

THE GRAVIMETRIC DETERMINATION OF SULPHUR IN CHROMIUM-VANADIUM STEEL WITHOUT A FUSION

Dissolve 4 or 5 grams of drillings in 200 c.c. of conc. nitric acid mixed with 100 c.c. of conc. hydrochloric acid. Mix the acids and let the mixture stand until it turns red, before putting it in the steel. Use an 800 c.c. beaker. After the action is over place the beaker on a graphite bath (see page 488) and heat without boiling. Stir the residue off the bottom of the beaker at intervals of a half hour. If, after an hour and a half of this digestion with the mixture of acids, the residue on the bottom of the beaker is not a clean yellow but still looks dark, especially in the layer touching the bottom of the beaker next to the glass, then a fresh mixture of equal quantity should be poured into the beaker and the stirring and digestion continued until the entire insoluble portion is a clear, bright yellow, putting in a third mixture if necessary. The decomposition having been effected, the contents of the beaker are transferred to a 600 c.c. casserole and evaporated on the graphite. Before the transfer to the casserole is made, 2 grams of sodium carbonate are added to the solution and stirred in well. Evaporate to dryness. Cool; add 100 c.c. of conc. HCl; cover; heat until all but the yellow residue of tungstic acid is in solution; evaporate again to dryness; dissolve as before with 50 c.c. of HCl and evaporate to 20 c.c. Add to the cool solution, 150 c.c. of water; heat and stir; add paper pulp and filter; wash with 1 : 40 HCl; add 20 c.c. of cinchonine solution and let stand for several hours, preferably until the next day, to remove the last traces of metatungstic acid; filter; wash with cinchonine water (5 c.c. of cinchonine solution to 500 c.c. of water) twenty times. Heat the filtrate and washings to boiling and precipitate the sulphuric acid formed with 25 c.c. of a saturated solution of barium chloride and finish the determination as in plain steels, page 335. This method is of course applicable to plain chromium steels and nickel-chromium steels which give low results with the ordinary evolution method as given for plain steels, when several per cents of either or both of these elements are present. The cinchonine solution referred to is given on page 131. Run blanks, repeating every operation, and deduct the sulphur so found.

THE DETERMINATION OF SULPHUR IN ALLOY STEELS, FERRO-ALLOYS, ORES, AND OTHER SUBSTANCES BY HEATING TO BRIGHT REDNESS, OR HIGHER, THE FINELY POWDERED BODY OR VERY THIN DRILLINGS, IN A STREAM OF HYDROGEN SATURATED WITH ACID

In 1909 the author of this book, see pages 49 and 177 of the first edition, called attention to the fact that only a portion of the sulphur is obtained by the evolution as ordinarily applied to plain carbon steels. In some highly alloyed steels, notably the chrome-tungsten steels, as little as one-twenty-fifth of the true sulphur is so found. The author had an experimental steel containing 0.250 per cent sulphur that showed but 0.010 per cent sulphur by the ordinary evolution method as given for plain carbon steels. This steel contained about 3 per cent chromium and 17 per cent tungsten and 0.49 per cent carbon.

The writer tried many schemes to overcome the failure of the evolution methods with no particular success until the autumn of 1911, when the following plan was worked out, which gives practically all of the sulphur by evolution as hydrogen sulphide.

It was while making some experiments for the determination of oxygen in metallic tungsten powder, that Mr. S. J. Lubowsky called the author's attention to the fact that hydrogen sulphide was being generated in the operation. He suggested that we might take advantage of the fact to determine the sulphur in our tungsten products. Acting on this suggestion, the author had him make a series of tests but it was found that only a small part of the sulphur known to be present was evolved, and that very slowly. After thinking the matter over, the author finally came to the conclusion that hydrochloric acid from the generator was also being carried by the hydrogen through the apparatus and that it must be a necessary part of the reaction. The apparatus was then so arranged that the H passed through a bubble tube containing HCl before it entered the furnace. An immediate speeding up of the evolution of the H_2S was noted and the full amount of sulphur was obtained on the sample of tungsten being tested.' It soon occurred to the author that all of the sulphur in barium sulphate could be obtained by the reaction,

$$BaSO_4+2HCl+8H=BaCl_2+4H_2O+H_2S.$$

This was speedily demonstrated. The H_2S began to appear in the cadmium chloride solution when the electric furnace had heated the tube containing barium salt to near a yellow heat. The author decided to use pure barium sulphate to standardize the iodine for titration of the H_2S. Practically the theoretical number of c.c. of the standard iodine were required, as will be shown. The same was found to be true of sodium sulphate:

$$Na_2SO_4+2HCl+8H=2NaCl+4H_2O+H_2S.$$

After some years' use of this method the following are the routine details for sulphur in steels containing much tungsten, or other alloys, etc.

Method.—From 0.100 to 1.000 gram is taken for analysis, depending on the sulphur content. A good rule is not to weigh more of the sample than will yield enough H_2S to consume 50 c.c. of the iodine standard. The sample should be finely divided, the finer the better. It should be spread out in as thin a layer as possible in the combustion boat. The boat should be located in the hottest part of the "combustion tube." When alloy or other steels are being run, 1 gram of drillings is weighed. The drillings or millings should not be over 60 mesh, or else should be thin curly drillings.

The sample is shoved into tube 5, Photo No. 5, page 124. The stopper at 5 is pierced with a five-sixteenths inch diameter quartz delivery tube that extends into the tube 5 to about the center and ends directly over the middle of the boat. This brings the acid and hydrogen directly to the sample and speeds up the reaction. (See drawing No. 3.) The combustion tube is supported in a slanting position to drain off any condensed moisture or acid toward the outlet end at 7. If this is not slanted in this manner the tube is liable to be cracked by moisture getting into the hot part. (See photo No. 5.)

The outlet end, being tapered, has no rubber stopper at 7, so that the bubble tube 8 is connected with the outlet of the evolution tube with a short piece of rubber tubing. A rubber stopper at this point is unsatisfactory, and practically out of the question, as it gives more or less sulphur. It was found important to avoid all cooling at the outlet, as low results were obtained when the outlet end was kept cold with wet wrappings.

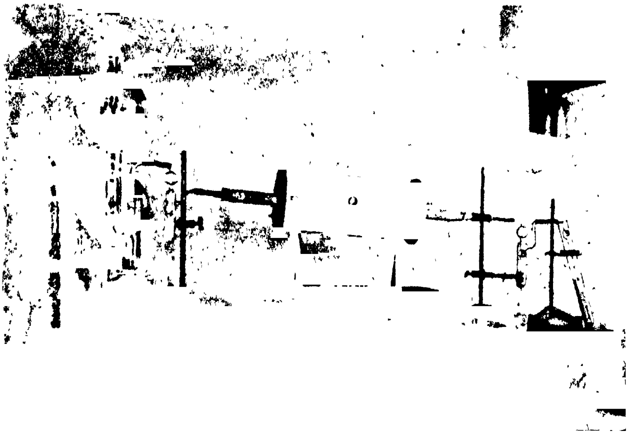
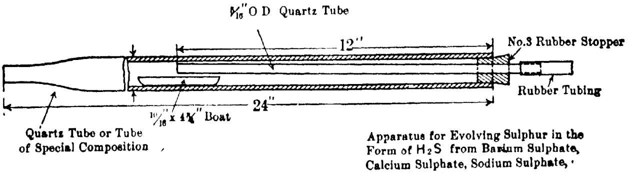


Photo No 5.



Apparatus for Evolving Sulphur in the Form of H_2S from Barium Sulphate, Calcium Sulphate, Sodium Sulphate, and other Substances

Drawing No. 3.

For this reason this end is allowed to get quite warm, but not hot enough to cause the rubber tube connecting with 8 to give up sulphur in the form of H_2S. All cooling devices must be omitted from 7 and are not needed at 5, unless a quartz tube

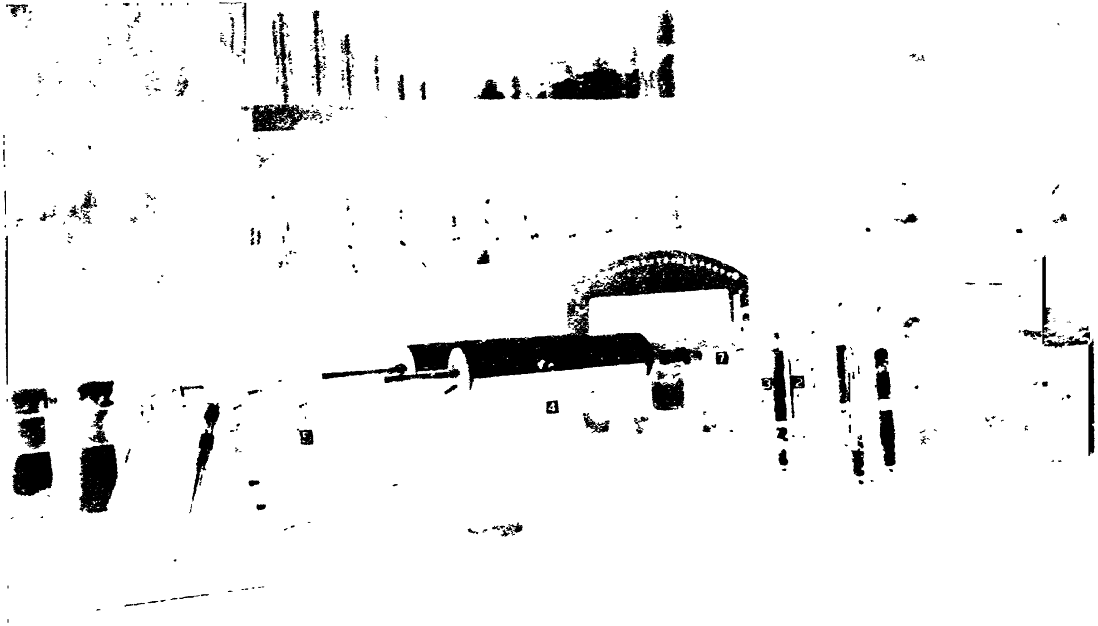


PHOTO NO. 6.

is used, as the *special composition tube conducts heat very much less than the quartz.*

The Kipp 1 contains the stick zinc, and 1 : 1 HCl. It is a 2 liter size. It is desirable to run two determinations at a time. The two furnaces are placed in parallel by distributing the hydrogen to both furnaces by means of a Y connection at 4. Photo No. 6 shows two determinations being run in two of the author's type of electric furnaces which he published several years ago in the Met. and Chem. Eng. It will be noted that it was necessary to have wet wrappings at the inlet ends of the tubes as quartz tubes were used at that time, 2 in Photo No. 5 is filled with stick KOH. 3 in Photo No. 5 contains a saturated solution of mercuric chloride to absorb any H_2S coming from the zinc, or tubing. It is filled with the mercury salt solution to the depth of about 1 inch; 4 contains a $1\frac{1}{4}$ inch layer of HCl of 2 : 1 strength, i.e., two parts of acid to one part of water. The purpose of this tube is to saturate the hydrogen with HCl before it enters the combustion tube at 5, Photo No. 5. The tube 4 should be refilled with fresh acid about every other time it is used. The tube 8 is empty and is used as a trap to catch any water or acid that distills over from 7. The 10×1 inch tube 9 contains the absorbing solution of the cadmium chloride, being of the same strength and amount as is used in the ordinary evolution method described on page 335 for the determination of sulphur in plain steel.

As stated, the finely powdered sample in the boat is shoved into 5, which should be nearly cold, or at least not hot enough cause to the hydrogen to explode. The boat is pushed into the hottest part of the tube at 6 in Photo No. 5. The furnace is of the same type as is used for carbon determinations.

When the tube is in place the stopper is inserted tightly into 5 and the stream of hydrogen is started through the apparatus. The hydrogen is passed through the tube for about twenty minutes to expel all air. The current is then turned on and the furnace is brought up to a yellow heat as quickly as possible. After the furnace has attained a yellow heat, the hydrogen is passed for an hour longer. With hydrogen still passing, the rubber connection is closed with a pinchcock just in front of 7. The first tube at 9 containing the bulk of the sulphur is removed and a similar tube is connected containing a fresh charge of the ammoniacal solution of cadmium chloride. If the conditions are observed, as given, as a rule but very little sulphide forms in the second tube at 9. But a third tube should be put in to make sure all of the sulphur has been evolved, especially when dealing with unusually high sulphurs or some substance like ferro-vanadium which yields all of its sulphur only after some hours' heating.

The contents of the various absorption tubes are poured through the same filter, beginning with the tube containing the least sulphide. The sulphur determination is then finished by iodine titration exactly as described for plain steels on pages 330-335.

Standardization of the Apparatus and the Iodine Solution with Barium Sulphate.—The author decided that the best standardization medium would be c.p. barium sulphate, and found that this salt is ideal for this work as its sulphur is readily converted under the conditions to hydrogen sulphide. The freshly ignited salt is weighed into a boat and shoved into the cold evolution tube and the process is then carried out as already outlined. The cadmium sulphide so obtained is titrated to get the sulphur value of the iodine standard. For the standardization it is convenient to weigh 0.020 gram of the barium sulphate. A blank is also put through. As a check standardization, one can use 0.010 gram of the $BaSO_4$. The blank is deducted and the number of c.c. of the iodine required to combine with hydrogen sulphide evolved from the barium salt is divided into the sulphur content of the barium sulphate used. For example, suppose it is found that a blank determination put through every operation consumed 1.8 c.c. of iodine and that 0.020 gram of the sulphate produced enough sulphide to consume 24.4 c.c. Then since barium sulphate contains 13.73 per cent sulphur, 0.02×00.1373 divided by 22.6 equals 0.000121, or 1 c.c. of the standard iodine equals 0.000121 gram of sulphur under the conditions as given.

Theoretically, a standard iodine containing 1 milligram of iodine per c.c. should be equivalent to 0.000126 gram of sulphur per c.c. of the iodine solution:

$$CdS+2HCl=CdCl_2+H_2S,$$

$$H_2S+I_2=2HI+S.$$

Therefore, 1 gram iodine $= \frac{S}{I_2}$, or $\frac{32.07}{253.84}$ or 0.126 gram of sulphur.

The following table gives results obtained on various substances by fusion with carbonate of sodium and niter, or by fusion with a mixture of sodium carbonate and sodium peroxide followed by solution in water and acid; evaporation; filtration and final precipitation with barium chloride, weighing the barium sulphate so found, being the gravimetric results. The same sample was also analyzed for its sulphur content by the evolution at a yellow heat in an atmosphere of hydrogen and HCl.

Sample	Result Obtained by Hot Tube Evolution Per Cent S	Result by Gravimetric Method Per Cent S	Kind of Material
H. S. steel bot. on the open market	0.076	0.076	18 per cent W 5 per cent Cr
"D—" H. S steel	0.085	0.083	High in Cr and W
No. 1501 H. S	0.069	0.064	High in Cr and W
No. 882 H. S	0.032	0.028	High in Cr, W and V
U. S. Govt. H S. std No. 31 of 0.019% S	0.020	0.020	High in Cr and W
Rex AA	0.029	0.030	High in Cr, W, and V
W. T. experimental steel	0.258	0.265	High in Cr and V
Tungsten powder	0.011	Trace	Tungstate of calcium
Scheelite	0.320	0.34	Portuguese
Wolframite	0.406 (with lime)	0.459	
Wolframite, D. C. N Z	0.718 (with lime)	0.716	
"P—" ferro-vanadium	0.150 (with lime)	0.148	
Sodium sulphate	22.64	22.56 (theoretical)	
Vanadate of iron	0.275 (with lime)	0.284	
Sodium uranate	0.094 (with silica)	0.093	
English ball clay	0.065	0.065	
Scheelite concentrates	0.996 (with lime)	0.891	Tungstate of calcium
New Jersey saggar clay	0.123 (with lime)	0.133	
Metallic tungsten powder lot No 1002	0.007	0.008	
Ferro-molybdenum	0.030	0.025	
Ferro-molybdenum	1.80	1.82	
Ferro-tungsten	0.175	0.180	

It is to be noted that those samples marked (with lime) were mixed with quicklime before reducing. If this precaution is omitted the results are far below the gravimetric figures. Also that ferro-vanadium gives up its sulphur very slowly, sometimes requiring as much as twenty hours before all of the sulphur is evolved. Sodium uranate must be mixed with considerable precipitated silica, or it will be exceedingly corrosive in its action on tubes and boats. Again, the method is not applicable as yet to arsenic sulphide, as much of the latter, probably all of it simply distills over undecomposed. Also some clays do not yield all of the sulphur for some reason not yet determined, but in spite of this fact the method is exceedingly valuable for approximate sulphur on all clays that the writer has tested, giving a quick commercial method for grading clays according to high or low sulphur rating.

The method is entirely accurate for all alloy steels, tungsten compounds, and molybdenum compounds and ferro-molybdenum and ferro-tungsten that the writer has thus far tested. He relies entirely on the method for these substances. Two or three hours being all the time required to evolve the entire sulphur. The work requires very little of the operator's time during the period of the evolution. The apparatus is inspected once an hour when a fresh absorption tube is set in place.

CHAPTER IV

PART IV

ANALYSIS OF LOW PER CENT TUNGSTEN STEELS

WHEN tungsten, phosphorus, and silicon are wanted in steels that contain from 3.0 to 3.5 per cent tungsten and less than 1 per cent chromium, dissolve 3 grams in 60 c.c. of 1.20 nitric acid in a No. 5 dish. Evaporate to dryness. Ignite to dull red. Cool and dissolve in concentrated hydrochloric acid, and finish as given under the analysis of high chromium-tungsten steels when silicon and phosphorus are wanted.

ANALYSIS OF ALL TUNGSTEN AND CHROME STEELS WHEN CHROMIUM AND TUNGSTEN, ONLY, ARE ASKED FOR

Third Method for Tungsten in Steel.—Dissolve 2 grams of sample in 30 c.c. 1 : 3 sulphuric acid. Heat until all action is over. Add 60 c.c. 1.20 nitric acid and digest at just below boiling until the residue in the 400 c.c. beaker is a clear yellow free of black particles. Dilute to 200 c.c. with water, and boil for twenty minutes. Add some paper pulp, filter out the main tungsten, and wash it free of iron test with dilute sulphuric acid. Dilute the filtrate to 500 c.c. and mix. From this solution fill a 250 c.c. flask to the mark.

First Portion.—Precipitate the remaining tungstic acid from this portion with cinchonine. Wash it free of iron-test with water containing cinchonine solution. Ignite it. Weigh and evaporate the weighed residue with a few drops of H_2SO_4 and about 10 c.c. of HF in the manner described on page 115, obtaining the tungsten in this portion as described. Multiply this portion of the tungsten by two and add this weight to that gotten from the main tungsten after it is purified. This main tungstic acid is ignited, weighed, the silica is removed by evaporation with a few drops of H_2SO_4 and 10 c.c. of HF. It is ignited at a low red and weighed again. Fuse it with twenty times its weight of sodium carbonate at a bright red heat; dissolve the fusion out in water; wash the insoluble thoroughly with water; ignite the residue on the filter until nothing remains but a brown residue; weigh this, deduct the weight from the silica-free weight of the main tungstic acid; to this remainder add twice the weight of the purified tungsten oxide obtained by cinchonine. This last total constitutes the total WO_3 which is converted to metallic tungsten by the factor .7931.

Second Portion.—Finish this for chromium as given under determination of chromium in chromium-vanadium steel, pages 5 and 10. If the chemist prefers to obtain the chromium by a separate analysis, he can get the total tungsten by one operation. The entire filtrate from the main tungsten residue is precipitated, without dividing it, by cinchonine. This precipitate is burned off with the main residue. The combined residues which constitute the total tungsten from 2 grams of sample are then freed from impurities in the usual way with bisulphate or sodium carbonate, and the total weight of pure WO_3 is multiplied by 79.31 and divided by the weight taken for analysis to obtain the per cent of tungsten. If the iron oxide is removed by sodium carbonate the silica is first removed by evaporation with hydrofluoric acid and sulphuric acid as given on page 115. The residue remaining after evaporation is ignited, weighed, and then the iron is removed by the carbonate fusion.

Cinchonine Solution.—Dissolve 25 grams of cinchonine in 200 c.c. of 1 : 1 hydrochloric acid.

Cinchonine precipitates tungsten almost instantly from moderately acid hydrochloric solution. It precipitates molybdenum after considerable lapse of time, and then only partially. At least, the above statement regarding molybdenum is correct if the attempt is made in the manner as given for tungsten. This constitutes a distinct difference between these two elements.

ANALYSIS OF CHROME-TUNGSTEN-VANADIUM STEELS FOR CHROMIUM AND VANADIUM

These elements are determined as in chrome-vanadium steels, boiling with sufficient excess of permanganate so that the tungsten residue looks brown from manganese oxide after twenty minutes' boiling. Filter on asbestos, or through a porous crucible and finish as usual. (See pages 5 and 10.)

THE ANALYSIS OF CRUCIBLE SLAG FROM TUNGSTEN-VANADIUM-CHROMIUM STEEL

Tungsten Oxide and Silica.—Fuse 1 gram of the finely ground slag with a mixture of 10 grams of sodium carbonate and 2 grams of potassium nitrate in a platinum crucible. Dissolve the melt in a platinum dish in water and transfer the solution and the insoluble matter to a 600 c.c. casserole; acidulate with an excess of HCl, about 75 c.c.; heat with the cover on until all effervescence is over, and evaporate to dryness on the graphite; heat with 30 c.c. of conc. HCl to dissolve the iron; then with 150 c.c. of water to dissolve the sodium salt; cool; add paper pulp; filter; wash with 1 : 40 HCl until free of iron test; hold this residue (A), as the main silicic and tungstic acids; the filtrate and washings from A are again evaporated to dryness; dissolved; filtered and washed as above; and the residue on the filter is designated as B. The filtrate and washings from B may still contain a little sodium metatungstate which is recovered by adding to the said filtrate and washings 10 c.c. of cinchonine solution; and, after stirring the same well, at least four hours are allowed to elapse before the tungsten cinchonate (C) is filtered out; washed with cinchonine water and burned off with B and A. The ash from A, B, and C contains all of the tungsten and silica. The latter is removed by evaporation with 15 c.c. of HF and 10 drops of conc. H_2SO_4 and ignition at a low red heat. The difference between the weight of the ash from A, B, C, before this evaporation and its weight after the evaporation and ignition, is calculated to percentage of SiO_2. The residue remaining after the evaporation with HF, etc., is fused with about twenty times its weight of sodium carbonate at a bright red heat for a half hour, or until all bubbling of CO_2 is over; is dissolved in water; the insoluble residue is filtered out; thoroughly washed free of salt; ignited; weighed; and deducted from the silica free weight of A, B, C. The remainder so obtained is figured to percentage of WO_3.

Oxides of Calcium, Magnesium, Manganese, and Iron.— Fuse 1 gram of the slag as above and proceed as directed up to the point where the filtrate and washings from B are obtained which will contain all of the Ca, Mg, Fe and Mn except a small amount remaining with the A and B. Fuse the ash from A and B with sodium carbonate as above, obtaining the water-insoluble residue which, after being thoroughly washed, is dissolved in HCl and added to the main filtrate from B. A double basic acetate separation of the iron from the manganese in this main filtrate is made as directed on pages 214 and 215. On the filter, after the second basic acetate separation, will be the iron, chromium, and aluminum, and some V. In the combined filtrates from the two basic acetate separations will be the manganese, calcium, and magnesium, which are separated and determined in the manner as given on page 135. Call the combined filtrates "X."

The acetates of iron, chromium, aluminum, titanium and part of the vanadium if present, are ignited and weighed at constant weight as Fe_2O_3 plus Al_2O_3 plus Cr_2O_3 plus TiO_2 plus some V_2O_5. These oxides are fused with twenty times their weight of sodium carbonate intimately ground with twice their weight of potassium nitrate to render the mixture of oxides soluble in acid. After keeping the melt in a molten condition for fifteen minutes, it is cooled and dissolved in water and acidulated with an excess of HCl; heated in the porcelain dish (to which the water solution of the fusion is transferred before the acidulation is made), until all effervescence is over; the cover is removed; more acid is added, if necessary, and all is concentrated until a complete solution of the oxides is effected. The solution is then diluted in a volumetric flask to 500 c.c. and 250 c.c. are converted into nitrates by evaporating twice to 20 c.c. with 50 c.c. additions of conc. nitric acid. This nitric solution is analyzed for vanadium as in ferro-vanadium; the vanadium found is calculated to V_2O_5, multiplied by two and deducted from the total weight of the Fe_2O_3 plus Al_2O_3 plus Cr_2O_3, etc., above mentioned. The other 250 c.c. are transferred to a liter boiling flask and peroxidized to remove the chromium and any vanadium in the manner described on page 179, until a filtrate is gotten that is free from any yellow color of chromium. The residue remaining on the filter after the final peroxidation will contain all of the iron except a film of the latter remaining in the peroxidation flask. The iron on the filter is dissolved off with 1 : 1 HCl and is combined with the small portion recovered from the flask by warming in it some 1 : 1 HCl. This total iron is free of chromium and vanadium and can be determined by reducing it with stannous chloride as in iron ores or it can be converted to sulphate and reduced with the zinc reductor and titrated with permanganate. The combined filtrates from the peroxidation contain all of the Al and Cr in one-half of the original 1 gram weight. The Al can be removed from the combined filtrates by adding 1 : 1 HCl slowly and with rapid stirring, until a turmeric paper no longer *immediately* changes to even a faint brown tint when dipped into the solution being neutralized. When the turmeric fails to change the solution is still alkaline enough to prevent any redissolving of the aluminum. The aluminum can then be filtered out and determined as given on page 36. The iron found as above is calculated to FeO by the factor 1.286 and multiplied by 2 being one-half the sample.

Chromium Oxide and Vanadium Oxide.—Fuse 1 gram of the ground slag in an iron crucible with 8 grams of sodium peroxide; dissolve out the fusion in water and boil for ten minutes in a casserole; acidulate with 150 c.c. of 1 : 3 sulphuric acid; boil with an excess of potassium permanganate and finish for chromium and vanadium as in steels. In order to fix the proper blank for the vanadium titration and to check the chromium determination, 330 mgs. of potassium dichromate and 60 mgs. of vanadium pentoxide of 99.7 per cent V were fused in the same way as the slag and put through all of the operations. It required 132.6 c.c. of the double sulphate standard to react with the chromium; therefore 0.330×0.3535 divided by 132.6 equals 0.00088 gram, or the value of the sulphate standard in chromium per c.c. The vanadium added, or 60×0.997, equals 0.0598 gram of V_2O_5. The percentage of V in the pentoxide being 56 per cent, there was present in the standard mixture 0.56×0.0598, or 0.0335 gram, V; 1 c.c. of the sulphate equals 0.00254 gram of V; therefore it will require 13.2 c.c. of this standard to equal 0.0335 gram of V. Now by actual titration 17.0 c.c. of the sulphate were used to obtain the blue end-point in the second part of the titration made after the addition of the ferricyanide as in steels; (see page 11) hence the blank to be applied to the analysis of the tests of the slag should be 17.00 c.c. less 13.20 c.c. or a blank of 3.8 c.c. A mixture of 380 mgs. of $K_2Cr_2O_7$ and 80 mgs. of V_2O_5 put through the fusion and all of the above operations gave a chrome value of 1 c.c. of the standard equals 0.00088 gram of Cr and a V blank of 4.0 c.c. The average blank is, therefore, 3.9 c.c. In this particular slag by the above method 2.90 per cent V and a check result of 2.92 per cent V were found, which multiplied by the factor of 1.627 gave a value in V_2O_4 of 4.71 per cent. The chromium found, using the above factor of 0.00088, was 11.76 per cent Cr and a check result of 11.88 per cent Cr giving an average of 11.82 which multiplied by the factor 1.461 equals 17.26, or the percentage of Cr_2O_3 in the slag.

Aluminum.—Having found the total iron by doubling that found in the 250 c.c. portion, it can also be calculated to Fe_2O_3; to the ferric oxide add twice the vanadic oxide found in the other 250 c.c.; to this sum add the chromic acid found in the separate portion: deduct the total of the three oxides from the total of the oxides of iron, chromium, aluminum, and vanadium (being the portion of the vanadium that may be carried along with the other oxides) and the remainder is calculated to percentage as Al_2O_3 plus any titanic oxide or phosphoric acid that may be present.

ANALYSIS FOUND

	Per Cent		Per Cent.
MnO	7.45	CaO .	2.27
FeO	14.53	MgO	0.98
Al_2O_3, etc .	9.88	WO_3 .	1.00
Cr_2O_3 . . .	17.28	SiO_2	41.78
V_2O_4.	4.71		

Ca, Mn, and Mg in Crucible Slag.—The combined filtrates "X" from the basic acetate separations of the "iron, chromium, and some V" (page 133) are made slightly ammoniacal and then an excess of ammonium persulphate or about 20 grams are added and the manganese is precipitated; the solution is heated until the precipitate separates well, leaving a clear supernatant fluid. A little ammonia is added from time to time to make sure that the solution is always faintly ammoniacal. The precipitate of hydrated oxide of manganese is filtered off; washed with water containing ammonia salt and a slight excess of ammonia. Call this filtrate and washings (A).

It is advisable to mix some paper pulp with the manganese precipitate to hasten the filtering and washing. The precipitate is then dissolved off the filter with a mixture of 30 c.c. of sulphurous acid water and 30 c.c. of 1 : 1 HCl. The paper and pulp is thoroughly washed. The pulp should be upset to make sure that none of the precipitate has escaped being dissolved. The top part of the pulp will frequently look free of the hydrates but underneath brown spots of the hydroxides will be found undissolved. Treat these spots with more of the mixture of sulphurous acid and hydrochloric acid. This solution and washings are reprecipitated as before with persulphate and ammonia. The precipitate is washed with ammonia salt and slightly ammoniacal water. Call this filtrate and washings (B). The washed precipitate is now dissolved off the filter with a measured amount of the standard sulphuric acid solution of ferrous ammonium sulphate. Upset the pulp in this case also, saving part of the standard mixture to dissolve any unattacked brown colored hydroxide spots that are found underneath in the pulp. Keep turning over the pulp during the washing also. In this manner the filter and pulp are thoroughly washed free of ferrous iron test, using ferricyanide to test for the presence of ferrous iron in the wash water. This solution and washings of the manganese are titrated to the first pink with standard $KMnO_4$. The number of c.c. of the ferrous standard measured, less the number of c.c. of the $KMnO_4$ standard used, multiplied by the manganese value of the sulphate standard per c.c. will give the number of milligrams of Mn found. This figure multiplied by the factor 1.291 gives the equivalent in MnO.

Standard Solutions.—The *ferrous ammonium sulphate standard* is made by dissolving 19.5815 grams of the c.p. salt in water; add to this 50 c.c. of 1 : 3 H_2SO_4 and dilute to 1 liter; 1 c.c. of this solution should equal about 0.00134 gram of metallic Mn.

The $KMnO_4$ standard solution is made by dissolving 1.58 grams of the c.p. salt in water and diluting it to 1 liter; 1 c.c. of this solution should be equivalent to 1 c.c. of the sulphate standard. Keep in the dark.

Calcium and Magnesium.—Combine filtrate and washings (A) and (B) and finish for these elements as described on page 431, beginning at the point where "the filtrates from the double precipitation of the iron are combined, evaporated to 600 c.c., heated to boiling, and the calcium is precipitated with 50 c.c. of a saturated solution of ammonium oxalate." The magnesium phosphate found in the filtrate from the lime is multiplied by the factor 0.36206 to convert it to MgO.

Phosphorus.—The phosphorus for the reasons given on pages 90–91 must be gotten by direct solution in the same manner as given for ferro-tungsten (see page 90) phosphorus determinations.

CHAPTER IV

PART V

DETERMINATION OF TANTALUM AND TUNGSTEN IN THE PRESENCE OF EACH OTHER APPLICABLE TO ORES, ALLOYS AND STEELS

ONE gram of sample is weighed into a platinum dish or its equivalent (platinum gold alloy will answer as a substitute for platinum ware in this work). Add about 50 c.c. of HF; then 5 c.c. conc. HNO_3, drop by drop, until action ceases in the case of ferro; in the case of ore, warm until all except perhaps a white residue is dissolved. Add 5 c.c. conc. H_2SO_4; evaporate to heavy white fumes; continue this fuming for some time; cool the dish; dissolve the contents in a mixture of 60 c.c. of HCl and 60 c.c. of water. Heat for about one hour on graphite bath; cool; mix considerable ashless paper pulp in the dish; filter; wash thoroughly with 1 : 30 HCl; this will require forty to sixty washings.

Hold this filter paper, marking it No. 1. To the filtrate from No. 1 add cinchonine solution; then let this filtrate stand overnight. Filter tungsten precipitate; wash with cinchonine wash; mark this filter paper containing the tungsten precipitate No. 2. Burn off papers No. 1 and No. 2 in platinum dish at a low heat. This residue constitutes the total tantalum and tungsten.

Put into this dish 10 grams of NaOH and 15 c.c. of water; heat on graphite bath for ten minutes; then boil for three minutes; cool; add 60 c.c. water; boil for one minute more and cool again. Transfer to 800 c.c. beaker. Dilute 400 c.c. with water. Filter out insoluble residue, mixing in with it considerable paper pulp before filtering. Wash with 1 per cent solution of NaOH; hold this paper, which contains the bulk of the tantalum. Make the NaOH filtrate and washings from the main tantalum acid with HCl; then make same just ammoniacal. Add 20 c.c. excess of ammonia; boil five minutes; filter; hold this filter paper, which contains the remainder of the tantalum. The filtrate from it is made acid with HCl; add 50 c.c. cinchonine solution and let stand overnight to precipitate the *main* tungsten, free from tantalum.

The two filters containing the total tantalum, together with a little tungsten, are burned in the same platinum dish at a low heat; cool; and extract as in the first instance with 10 grams NaOH and 50 c.c. of water; filter, washing thoroughly with NaOH wash. This will remove any small amount of tungsten that may have been retained in No. 1 and No. 2 precipitates. Mark this paper (A). The filtrate from (A) will contain the small amount of tungsten and also may contain a little tantalum dissolved by the NaOH.

Filtrate from (A) is made acid with HCl; then ammoniacal, using an excess of 20 c.c. of ammonia; boil five minutes; filter off small amount of tantalum, if any; wash with ammonia wash twenty times and mark the paper (B).

Filtrate from (B) is made acid with HCl, 50 c.c. cinchonine added and allowed to stand overnight. Filter off both the main and the small amount of tungsten obtained by the two cinchonine precipitations on the same filter; wash with cinchonine wash: burn off in a weighed platinum crucible or its equivalent; remove the silica as usual with HF containing sufficient sulphuric acid, that is, three or four drops of conc. sulphuric acid. Drive off excess H_2SO_4 as usual; ignite to a low red heat and weigh. This weighed residue is fused with 15 grams Na_2CO_3. Dissolve the melt in a platinum dish in water and transfer the contents of the platinum dish to 600 c.c. beaker; make acid with HCl and then ammoniacal with 5 cc. excess of ammonia; boil; filter; wash forty times with 1 : 1 NH_4OH. Burn off the washed paper in a platinum crucible until char is all gone; weigh. The difference between this weight and the previous weight gives the pure WO_3.

Filters marked (A) and (B) are now combined; burned off in a platinum dish with 50 c.c. of HF and 5 c.c. conc. H_2SO_4. Evaporate this mixture until the residue appears to be the condition of a moist solid. Dissolve this solid in a mixture of 70 c.c. of water and 30 c.c. HCl; heat for twenty minutes on a graphite bath. Mix in, about an equal bulk of paper pulp;

filter; wash thoroughly with 1 : 30 HCl. Hold this filter paper pulp; let the filtrate stand overnight, as frequently some tantalum will separate out in filtrate and washings after standing some hours.

If any precipitate forms, filter and wash as above. Combine this paper with the paper pulp filter; burn off paper and weigh again. If the residue is not pure white, dissolve again in 50 c.c. of HF and 5 c.c. H_2SO_4 conc.; evaporate as before to a solid; dissolve this solid as before in 30 c.c. HCl conc. and 70 c.c. of water; filter; burn off and weigh again, when the residue should be pure white or nearly so, constituting the total tantalum oxide plus any niobium that may be in the ore or alloy.

No attempt is made in this method to separate tantalum from niobium. It is assumed that these elements are both present in this residue.

THE ANALYSIS OF TANTALUM ORE AND FERRO-TANTALUM WHEN SILICA IS NOT REQUIRED

This is a simple proposition both in the ore and the ferro on account of their ready solubility in HF. Indeed the tantalum content can be obtained in three or four hours. Weigh into a platinum dish of about 150 c.c. capacity, 1 gram of the finely ground ore; pour upon it 20 c.c. of HF, c.p. grade, and then add conc. nitric acid, a drop or two at a time, until all action ceases, which is vigorous in the case of a ferro; add in all 5 c.c. In ores 1 or 2 c.c. of the nitric is sufficient, as no action takes place.

Now add 5 c.c. of conc. H_2SO_4 and evaporate on a graphite bath until no more fumes of SO_3 are formed. Add 30 c.c. of conc. HCl and 70 c.c. of water and heat for an hour. Filter on a double 11 cm. paper, wash forty times with 1 : 20 HCl and ignite at a low red heat in a weighed platinum until white; cool and weigh; calculate the Ta_2O_5 so obtained to metallic tantalum in a ferro by use of the factor 0.8194. The foregoing scheme assumes the absence of tungsten, and that no attempt is made to discriminate between tantalum and niobium.

The tantalic acid obtained will contain all of the tungsten present as the method is the same as the one given for the latter element on page 74. To separate the tantalum from the tungsten, use the sodium hydroxide extraction method as given on pages 138–139. Mr. Eugene Fleck of this laboratory worked out the hydroxide extraction method.

SILICON IN FERRO-TANTALUM AND TANTALUM ORE

Fuse the finely ground substance in an iron crucible with a mixture of sodium peroxide and sodium carbonate in the same manner as given for gravimetric sulphur in ferro-titanium-silicon-aluminum on page 47. Dissolve out the fusion in water; acidulate it with HCl after transferring the water solution to a casserole or porcelain dish; heat until the iron is dissolved; add about 40 c.c. of 1 : 3 sulphuric acid; evaporate to thick fumes; cool; add water; heat until all iron sulphate is dissolved; filter off the insoluble residue, which should contain all of the tantalum and silicon. Wash free of iron; ignite; weigh as oxide of Ta, W, and Si. Evaporate with 15 c.c. of HF and 2 c.c. of conc. H_2SO_4. There must be an excess of sulphuric acid or tantalum fluoride will be volatilized as a white sublimate. Ignite at a low red, after evaporation to dryness. Loss of weight is silica. The residue in the crucible will constitute the total tantalum plus all of the tungsten if cinchonine is used on the filtrate from the insoluble residue and any precipitate so found is burned off with this last residue. This total Ta and W residue can then be finished for these two elements as previously described. Run blanks on all operations for silica and deduct the silica so found.

The following recoveries were made by adding known amounts of tantalum in the form of ferro-tantalum, also in known mixtures of tantalum and tungsten ore. The following amount of tungsten was added to ferro-tantalum:

Tungsten in Mixture No. 1

Added	Found
0.1700 gram W	0.1683 gram W
0.1700 gram W	0.1705 gram W

Tantalum in Mixture No. 1

0.6300 gram Ta	0.6300 gram Ta
	0.6300 gram Ta

Tungsten in Mixture No. 2

Added	Found
0.0170 gram W	0.0174 gram W

Tantalum in Mixture No. 2

0.6300 gram Ta	0.6270 gram Ta 0.6280 gram Ta

Tungsten in Mixture No. 3

0.0085 gram W	0.0095 gram W

Tantalum in Mixture No. 3

0.6300 gram Ta	0.6210 gram Ta 0.6260 gram Ta

Mixture W and Ta Ores

Mixture No. 1

0.250 gram tantalum ore of 75.0 per cent Ta_2O_5
Recovery of Ta_2O_5 from Mixture No. 1

0.1875 grams Ta_2O_5 added
0.1900 grams Ta_2O_5 found
0.1900 grams Ta_2O_5 found

0.750 gram tungsten ore of 68.0 per cent WO_3
Recovery of WO_3 from Mixture No. 1.

0.5100 grams WO_3 added
0.5105 grams WO_3 found
0.5158 grams WO_3 found

Mixture No. 2

0.750 gram tantalum ore of 75.0 per cent Ta_2O_5
Recovery of Ta_2O_5 from Mixture No. 2

0.5700 grams Ta_2O_5 added
0.5800 grams Ta_2O_5 found
0.5700 grams Ta_2O_5 found

0.250 gram tungsten ore of 68.0 per cent WO_3
Recovery of WO_3 from Mixture No. 2

0.1700 grams WO_3 added
0.1700 grams WO_3 found
0.1720 grams WO_3 found

Tantalum in Steel.—Dissolve 3 grams exactly as for tungsten in high speed steel (see page 114). Finish as for tungsten up to the point where the silicon is removed with HF and sulphuric acid. The ignited residue will contain all of the tungsten, if any be present, and all of the tantalum. This residue should be ignited at a very low red heat only; just hot enough to remove all of the filter char. This evaporation and ignition should be done in a platinum dish for convenience. Extract the residue with NaOH as described for Ta in alloys and finish for Ta and W as therein described (page 138).

CHAPTER V

PART I

MOLYBDENUM POWDERS

Carbon.—Carbon is obtained by direct combustion in a stream of oxygen, using the electric furnace with temperature between 900° and 950° C. Decarbonization takes about a half hour. Use some red lead when the silicon content is high; 2 grams of the former per gram of Mo.

Phosphorus.—If any molybdic acid separates out during the course of a determination of phosphorus as in steels, it is certain to carry phosphorus out with it as phospho-molybdic acid, in the same way that tungsten does. In such cases, dissolve the ferro or powder in a mixture of equal parts of conc. HCl and HNO_3. Take 0.813 gram of the sample; dissolve it in 100 c.c. of the mixture; heat until all action is over; add 100 c.c. of conc. HCl; heat with the cover on until action is over and evaporate to 25 c.c. Dilute to 400 c.c. and remove the bulk of the molybdenum with H_2S. Filter; wash; and evaporate the filtrate and washings to 20 c.c. Add 100 c.c. of conc. nitric acid; heat with cover on until action is over and evaporate to 25 c.c. Transfer to a 150 c.c. beaker; dilute to 40 c.c.; boil with a slight excess of $KMnO_4$ and finish as in phosphorus in steel.

Silicon.—Dissolve 1.5 grams in 60 c.c. 1.20 nitric acid. Add 120 c.c. of 1 : 3 sulphuric acid. Evaporate in a porcelain dish on graphite or sand bath to thick white fumes of sulphuric anhydride. Cool and add 80 c.c. 1 : 1 hydrochloric acid. Boil five minutes. Cool again and add 50 c.c. of water. Mix in some paper pulp and filter on an 11 cm. double ashless filter. Wash free from iron test with 1 : 10 hydrochloric acid. Then wash free from chloride test with distilled water. Ignite in a platinum crucible at the faintest red heat until white. Weigh and evaporate with hydrofluoric acid and a few drops of sulphuric acid.

Ignite again at lowest visible redness. Calculate the loss of weight as usual to silicon.

Molybdenum.—*First Method.*—Fuse 0.500 gram of finely ground powder with twenty times its weight of sodium carbonate plus 2 grams of potassium nitrate. Heat cautiously until the fusion is free from black particles. Dissolve the melt in a platinum or porcelain dish (platinum preferred) with water. Remove the platinum crucible from the dish and rinse it off carefully, allowing the washings to run on the filter through which the water solution is to be poured. Mix the water solution of the fusion with a little paper pulp and filter it through the filter aforesaid. Wash the residue forty times with dilute sodium carbonate water. The residue on the filter contains all of the iron and copper present in the metal, a little platinum oxide from the crucible, and a little molybdenum (see page 146).

The filtrate and washings are transferred to an 800 c.c. beaker. Two grams of tartaric acid are added. The solution is acidulated with sulphuric acid in *slight* excess. The acidulated solution is heated for twenty minutes to expel the major portion of the carbon dioxide. It is then cooled; three drops of phenolphthalein solution are added. (See Phosphorus in Steel, p. 318.) A rather concentrated solution of sodium hydroxide is added until one drop produces a pink color. Next add 1 : 3 sulphuric acid until one drop causes the solution to become colorless. Dilute to 700 c.c. with water. If the attempt be made to precipitate molybdenum in too acid a solution, by hydrogen sulphide, the former is partially reduced to a blue oxide and partially precipitated as sulphide. To avoid this highly undesirable condition it is merely necessary to keep the solution but very slightly acid until it is well saturated with H_2S. It then turns to a deep orange colored fluid from which the molybdenum is quickly precipitated, by the addition of 6 or 7 c.c. of 1 : 3 sulphuric acid, as a brown sulphide. Pass the gas for thirty minutes longer. Add paper pulp to the beaker, mixing it well with the sulphide just before passing the gas for the half hour as directed. In this way the precipitation is rapid. The sulphide can be filtered and washed quickly. It is washed with H_2S water containing two drops of 1 : 3 sulphuric acid per 500 c.c. of wash water. Give the sulphide forty washings, permitting each washing to drain off thoroughly before the succeeding one is applied. The sulphide is then roasted just below redness in a platinum or porcelain crucible. The contents of the crucible can be ignited without loss of molybdenum trioxide, but the crucible must not be allowed to exceed the faintest visible redness. The MoO_3 usually burns to a brownish white residue, owing to traces of impurities.

After weighing the oxide it is extracted with 1 : 1 ammonia (11.50 per cent) on the water bath until there remains but a small residue, consisting of traces of iron and some silica. This is mixed with a little paper pulp, filtered and washed thoroughly with dilute ammonia water.* It is ignited, weighed, and its weight is deducted from the first weight of the MoO_3. The remainder is multiplied by 66.66 (or $\frac{2}{3} \times 100$) and divided by the weight taken for analysis to obtain the per cent of molybdenum in the sample. The filtrate and washings from the sulphide precipitation should always be tested by passing H_2S through it for an hour more to make sure that no further precipitation of molybdenum sulphide will occur. If the directions as given are carefully followed, no molybdenum will be found at this point.

Second Method.—Completely soluble molybdenum can be examined for molybdenum as follows: Dissolve 0.400 gram of finely ground sample in 30 c.c. of 1.20 nitric acid. Cool and add 2 grams of tartaric acid. Then add an excess of ammonia. Drop in 1 : 3 sulphuric acid until the solution is just faintly acid. Dilute to 300 c.c.; precipitate with hydrogen sulphide; and finish for molybdenum as given in the first method.

Iron.—The residue of iron, etc., remaining on the filter from the water solution of the sodium carbonate and niter fusion is dissolved off with a little hot 1 : 1 hydrochloric acid. The filter is washed free from iron test. This filtrate and washings are almost certain to contain some molybdenum. (The writer has found molybdenum with the iron, even after it has been fused a second time with sodium carbonate.) Add dilute ammonia to the solution a drop at a time until the iron hydroxide appears. Then add sulphuric acid (1 : 3) until the iron precipitate just dissolves. Dilute to 300 c.c. with water. Pass H_2S. The small quantity of molybdenum quickly separates. It is filtered out and washed in the same manner as the main sulphide precipitate. Ignite this sulphide to oxide, weigh it, extract it with ammonia in the same way as the main oxide. Filter out the insoluble matter, and wash it with dilute ammonia. Ignite it, weigh it, and deduct the weight from the first weight; calculate the remainder to Mo, and add it to the principal part of the molybdenum found. The filtrate and washings from the small sulphide precipitate contain all of the iron which can be determined by evaporation to a small volume with a slight excess of potassium chlorate; 1 or 2 grams should suffice. Then add an excess of 1 : 3 sulphuric acid and evaporate to thick, white fumes of sulphuric anhydride. Dilute with water. Reduce with zinc reductor (see page 366) and finish by titration with permanganate solution.

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* If this filtrate and washings are blue estimate the copper therein with KCN as in steels, page 206, calculate the copper found to CuO and deduct the result from the weight of the impure MO_3.

Tungsten.—Evaporate the filtrate and washings from the main sulphide precipitate obtained by the first method to moist dryness. Add 100 c.c. of conc. nitric acid. Heat with cover on until all action is over. Remove the watch glass from the casserole and evaporate again to moist dryness. Add water; heat until all salt is in solution; filter out the insoluble residue; wash it free from salts with 1 : 20 hydrochloric acid. This will take about forty to fifty washings. Evaporate the filtrate and washings again to moist dryness, and add 100 c.c. of conc. hydrochloric acid. Heat with the cover on as before, and evaporate a third time. Add water and 20 c.c. of cinchonine solution; warm for a short time to permit any small precipitate of tungsten to form and settle; wash it with a mixture of 50 c.c. of HCl, 400 c.c. of water, and 5 c.c. of cinchonine stock solution, which consists of 25 grams of cinchonine dissolved in 200 c.c. of 1 : 1 HCl. Add this washed paper to the first one obtained after evaporation of the nitric solution to moist dryness, adding water; heating; and filtering out the insoluble residue and washing it free of salts. Ignite the two papers; weigh the ash so obtained as WO_3+SiO_2. Finish as given for tungsten in steels from this point by evaporation with a few drops of conc. H_2SO_4 and 10 c.c. of HF, etc.

SULPHUR BY EVOLUTION IN A STREAM OF HYDROGEN SATURATED WITH HCl, HEATING TO ABOUT 900° C.

Evolution

For a description of this method, which is by far the most satisfactory for tungsten and molybdenum powders and for ferro-tungsten and ferro-molybdenum, read pages 122-129. Use 1 gram of the finely divided substances and proceed as directed. If there be any sulphates present they too will be decomposed by the reaction:

$$Na_2SO_4+2HCl+8H=2NaCl+H_2S+4H_2O.$$

Gravimetric Method

Fuse 2 grams of the powdered substance with 20 grams of sodium carbonate and 4 grams of potassium nitrate in a platinum crucible. (Or fuse in an iron crucible with Na_2CO_3 and Na_2O_2 in the same manner as given on page 47 for ferro-titanium-aluminum-silicon.) The sodium carbonate and niter fluxes are ground thoroughly together in an agate mortar. Heat until the melt in the platinum crucible is a clear yellow, free of dark specks. This requires but a few minutes. Dissolve the melt in water; transfer it to a casserole. Make just acid with 1 : 1 HNO_3; then add a few c.c. in excess and warm a while to coagulate the MoO_3 that separates; filter it out; wash it fifty times with dilute (1 : 10) nitric acid. (If the bulk of the molybdic acid is not removed by filtration, some of it will be found with barium sulphate at the end of the analysis, causing high results. In any case it is safer to fuse the final barium sulphate with Na_2CO_3; dissolve the fusion in water; make it slightly acid with HCl; warm; and pass H_2S until saturated. If any sulphide forms it should be filtered out; and finished for molybdic oxide in the usual way; deduct its weight from the weight of the barium sulphate found.)

After the main molybdic acid has been filtered out and washed, as described at the start, the filtrate and washings from it are evaporated low, and concentrated HCl is added cautiously a little at a time; heat with each addition of the acid to permit the effervescence to occur in installments; when no further reaction occurs, add 50 c.c. excess of the conc. HCl and evaporate to dryness on a graphite bath or hot plate. Add 40 c.c. of

1 : 1 hydrochloric acid. Heat with the cover on for a half hour. Add water and heat again. Filter and wash with 1 : 20 hydrochloric acid, forty times. Heat the filtrate to boiling, and precipitate with barium chloride solution, adding the latter in excess, about 50 c.c. of the saturated solution. Let the test stand overnight; filter out the barium sulphate; wash it with water containing a drop or two of HCl to 500 c.c. about twenty times; and then free of chlorine test with water only. Ignite the washed barium sulphate in a platinum crucible until it is white. Moisten it with a drop or two of 1 : 3 sulphuric acid and ignite it again and weigh. Multiply the weight so obtained by the factor .1373×100 and divide by the weight taken. This final result will be the per cent sulphur.

Manganese.—Proceed as in steels or ferro-vanadium, dissolving the powder in 1.20 nitric acid.

Copper.—Nitric acid solutions of molybdenum are precipitated but slightly, even after one hour's standing, by potassium ferricyanide. This reagent affords a rapid means of determining the amount of copper that may be present in the molybdenum. Dissolve 1 gram of sample in 30 c.c. 1.20 nitric acid. Add ammonia until the iron hydroxide forms. Then add sulphuric acid (1 : 3) a few drops at a time until the hydrate of iron is just dissolved; then add 10 c.c. excess of the acid, as copper ferricyanide precipitates better if there is some free acid. Now precipitate the copper with 20 c.c. of the same potassium ferricyanide solution used to separate copper in ferro-vanadium. If the copper in solution is likely to exceed 10 mgs., then add an additional 2 c.c. of the ferricyanide solution for every milligram of copper in excess of 10 mgs. Finish as given in the author's method for copper in steel. The analysis of ferromolybdenum is similar to that of the powders.

TYPICAL ANALYSES

		Carbonless
	Per Cent	Per Cent
Carbon	4 60	0 07
Manganese	0 03	0 18
Phosphorus	0 029	0 059
Sulphur	1 02	
Silicon	0 50	2 88
Molybdenum	90 00	92 50

CHAPTER V

PART II

THE ANALYSIS OF FERRO-MOLYBDENUM

DISSOLVE 0.4 and 0.5 gram for a check in 50 c.c. of 1.20 nitric acid to a clear solution. Dilute to 200 c.c.; add a considerable excess of ammonia and precipitate the iron. Filter it out; wash it with ammonia. Redissolve this iron in 50 c.c. of 1 : 1 HCl; reprecipitate the iron again, washing as before with dilute ammonia wash. The iron hydroxide is dried; ignited at a low heat; and weighed as Fe_2O_3+some MoO_3 and a little SiO_2. The residue in the crucible is dissolved in HCl; the silica is filtered out; washed; weighed and deducted from the total weight of the oxides of iron, etc. The filtrate from the silica is made nearly neutral and the molybdenum therein is precipitated with H_2S in hot solution; filtered out; washed with H_2S water; ignited at a very low red heat; weighed and deducted from the iron oxide, etc., giving a remainder consisting of Fe_2O_3 plus any phosphoric acid that may have been carried out with the iron oxide. This phosphoric acid can be found by evaporating the filtrate from the above molybdenum sulphide to low volume; convert to nitrates and finish the phosphorus as in steels. The phosphorus so found is calculated to P_2O_5 and deducted from the weight of the P_2O_5 plus Fe_2O_3, leaving a remainder that can be calculated to metallic iron. This phosphorus is not necessarily the total phosphorus. The latter can be determined on a separate portion as described under Phosphorus in Molybdenum Powder.

The main portion of the molybdenum is contained in the two sets of filtrates and washings from the precipitation and the reprecipitation of the iron by ammonia as given above. These filtrates and washings are combined; made slightly acid with HCl and the Mo is separated with H_2S; washed; ignited and weighed as MoO_3 plus any little silica present which is removed by dissolving the MoO_3 in conc. ammonia and warming until only a small floating residue remains which is filtered out; washed with ammonia water; ignited; weighed; and deducted from the first weight of the main MoO_3. The remainder plus the MoO_3 found with the iron, as already described, constitutes the total MoO_3 which is calculated to Mo by the factor 0.6666.

Silicon.—This element can be determined on the same portion as is used for the molybdenum if the nitric acid solution is taken to dryness on the graphite bath. Do not ignite the dish over a bare flame, as in tungsten, as there is danger of loss of the Mo by volatilization. Dissolve the dry residue in 50 c.c. or more, if necessary, of conc. HCl; dilute; filter; wash with dilute HCl; wash until the residue on the filter no longer gives a test for iron; evaporate the filtrate and washings again to dryness; dissolve; filter; wash as before; combine the two filters from the first and second evaporations; ignite the same at a very low red heat and weigh as SiO_2 plus a little MoO_3. For close work this silica should be fused with ten times its weight of sodium carbonate; the fusion dissolved in HCl and evaporated twice to dryness as before, finally weighing as pure silica.

Fe+Mo.—The filtrate from the second evaporation to dryness in the presence of the main iron and Mo can be combined with the filtrate and washings from the evaporation of the acidulated sodium carbonate fusion of the impure silica. The combined filtrates contain the total iron and Mo and can be analyzed for these elements as already given under Ferro-Molybdenum.

The carbon, manganese, tungsten, and sulphur are determined as given for Molybdenum Powders.

RESULTS OBTAINED ON A HIGH CARBON TYPE

	Per Cent		Per Cent
Carbon	3 66	Silicon	0 86
Manganese	0 13	Iron	23 26
Phosphorus	0 035	Molybdenum	71 30

THE ANALYSIS OF FERRO-MOLYBDENUM-TUNGSTEN

Tungsten, Phosphorus, and Silicon.—Dissolve 1 gm., and $1\frac{1}{2}$ grams for a check, in 50 c.c. of 1.20 nitric acid in a No. 5 porcelain dish; evaporate dry but do not ignite with a bare flame. Redissolve with 100 c.c. of conc. HCl; evaporate dry; dissolve in 50 c.c. of conc. HCl and evaporate to 20 c.c.; add 25 c.c. of water; heat twenty minutes; filter; wash with 1 : 40 HCl; evaporate the filtrate and washings to 10 c.c.; add 25 c.c. of water; heat and filter out any small residue of tungstic acid that may have separated out after this second evaporation. The filtrate and washings from this last evaporation are then converted to nitrates and finished as described on pages 41-46.

The residues on the filters from the above first and second evaporations to dryness contain all of the tungsten, silicon, and a little of the molybdenum. These papers are ignited at a low red heat until the carbon is gone; add 10 grams of anhydrous sodium carbonate to the ash and fuse to a clear liquid that no longer gives off any bubbles of CO_2. Dissolve out this fusion; acidulate it with HCl and evaporate to dryness, after all effervescence and spraying are over, in the covered casserole. If the fusion is dissolved out in porcelain, the solution must be made acid with HCl as the dissolving of carbonate fusions with water alone in porcelain dishes causes the latter to be attacked and silicon results to be too high, especially if heat is applied to hasten matters.

After the evaporation to dryness the residue is redissolved in HCl; add water; filter out the tungsten; wash it as before; evaporate the filtrate and washings again to dryness; dissolve; filter; and wash. This second filtrate and washings will contain some tungsten which must be removed by cinchonine; heat the filtrate before adding the cinchonine; filter out the tungsten so precipitated; wash it with cinchonine water; combine this filter with the two residues obtained from the evaporation of the above fusion twice to dryness and burn all in a platinum crucible to a yellow residue free from the carbon of the filters; weigh it as WO_3+SiO_2. Remove the silicon by the usual evaporation with HF and H_2SO_4, calculating the loss of weight as the silicon of the alloy. The residue in the crucible is calculated to tungsten by the factor 0.7931.

Molybdenum.—Fuse 0.5 gram of the finely ground alloy in a platinum crucible with an intimate mixture of 10 grams of sodium carbonate and 0.5 gram of niter until a quiet fusion is obtained and then continue to maintain the fusing temperature for ten minutes more. Dissolve the fusion out in water; filter out the insoluble residue of iron and manganese; wash it with sodium carbonate water; ignite it; grind it in a small agate mortar; return the fine powder again to the crucible; clean the mortar by grinding it out with a little sodium carbonate; return this carbonate to the crucible; again grind some fresh carbonate in the mortar, and so on, until the carbonate no longer shows a change of color when ground in the mortar Grind 10 grams of carbonate with 0.200 gram of niter for this second fusion which is made and dissolved out as in the first fusion. The filtrates and washings from insoluble residues obtained after each fusion contain all of the molybdenum and tungsten from the alloy. The first filtrate and washings contain practically all of these elements. Add to it 2 grams of tartaric acid and two drops of methyl orange solution (1 gram of the methyl orange dissolved in a liter of water). Now add HCl until one drop just turns the solution pink. Pass H_2S through the solution when it will turn a deep red due to the combination with the H_2S; the addition of a few drops of HCl will cause the molybdenum sulphide to then precipitate out promptly and perfectly after a thorough saturation with H_2S. The directions must be carefully followed for if the attempt is made to precipitate molybdenum from a solution containing much free acid, a blue filtrate is obtained which contains much of the molybdenum in a reduced form that is very unsatisfactory to handle, as explained on page 156. Wash the molybdenum sulphide, so obtained from both sets of filtrates and washings, thoroughly with H_2S water; ignite it at a low red heat and weigh; dissolve this MoO_3 in ammonia; filter the solution; wash the filter thoroughly with ammonia; ignite it; weigh it; deduct this weight from the first weight of the MoO_3 and calculate the difference in weight to molybdenum by the use of the factor 0.6666.

Iron.—The insoluble residue obtained from the second fusion with sodium carbonate and niter contains all of the iron free from tungsten and Mo and is especially convenient for the iron determination as the two latter elements must be separated before the iron can be determined. Dissolve this residue, after burning off the paper in the crucible in which the fusion was made, in conc. HCl; clean the iron stains from the crucible with this acid; precipitate the solution of the residue and the cleanings of the crucible with ammonia; redissolve; reprecipitate, and redissolve it again to remove any platinum; then reduce the solution with stannous chloride and finish for iron as in iron ore by titration of the reduced iron with potassium dichromate. (See page 442.) Or convert to sulphate by taking to fumes with H_2SO_4. Redissolve; dilute; pass through reductor and finish as given on page 443.

Sulphur.—The best and easiest way to get the sulphur is to evolve it from a hot tube by the method given on page 122. Or the sulphur can be determined by any of the methods given on pages 148 for molybdenum powders.

GRAVIMETRIC SULPHUR IN FERRO-MOLYBDENUM BY DIRECT SOLUTION IN ACIDS

Heat 5 grams of the powdered sample in 250 c.c. conc. HNO_3. When action is over and red fumes are all gone, dilute with 200 c.c. of water; filter off the molybdic acid that separates at this stage and wash it fifty times with dilute HNO_3. If the bulk of the MoO_3 is not filtered out here, some of it will be found with the barium sulphate at the end of the analysis, causing high results. Transfer the filtrate to a No. 7 dish; add 2 grams of Na_2CO_3 and evaporate to dryness. Redissolve in 75 c.c. of conc. HCl, and evaporate to dryness again. Redissolve in 20 c.c. of conc. HCl, and when all the iron is in solution add 100 c.c. of water, stir it well, heat it for a while, filter it and wash it with dilute HCl. Add to the filtrate and washings 20 c.c. of conc.. HCl; dilute with water to 400 c.c. volume; heat to boiling and add 25 c.c. of a saturated solution of $BaCl_2$; let stand twelve hours. Filter off the barium sulphate; wash it free of iron with water containing a few drops of 1 : 1 HCl, and then free of chloride with water only.

Ignite it in a weighed platinum crucible; moisten it with two drops of sulphuric acid to convert any barium sulphite, formed by the reducing action of the burning filter paper, to barium sulphate; when the fumes of sulphuric acid are gone, heat the crucible to redness. Cool it; and weigh it; calculate the per cent of sulphur by multiplying the weight of the barium sulphate found by 13.73 and dividing by the weight taken for analysis. Blanks should be run covering all operations and any sulphur so found, deducted.

CHAPTER V

PART III

MOLYBDENUM IN HIGH-SPEED STEELS AND ORES

(Presence of Much Tungsten)

WEIGH 2 and 3 gram samples into No. 5 porcelain dishes; dissolve in a mixture of 30 c.c. HCl (1 : 20) and 30 c.c. HNO_3 (1 : 42); heat moderately until residue is yellow; rinse covers with water; add 100 c.c. HNO_3 (1.42). Take to dryness on graphite bath over low flame; bake at 500° to 550° C. for ten minutes. Let cool, add 40 c.c. conc. HCl and heat until all is in solution except yellow residue. Add 50 c.c. distilled water; stir in paper pulp; filter through double 11 cm. papers into 600 c.c. beakers and wash forty times with 1 : 10 HCl, getting filtrate (A).

The principal part of the molybdenum, i.e., in (A), is separated as follows: Add ammonia to it until a precipitate forms that no longer dissolves on stirring. Add 1 : 3 acid until this precipitate *just* dissolves. Then saturate the *nearly neutral* solution with hydrogen sulphide, and obtain the molybdenum sulphide. If the solution containing the molybdenum is too nearly neutral, H_2S causes only a deep red coloration in it; if the solution is too acid, the passage of the hydrogen sulphide results in a partial precipitation of the molybdenum together with a blue coloration. From the red solution, the molybdenum is easily precipitated by a *very slight* addition of acid. Add the latter cautiously, a c.c. or two at a time, until the molybdenum begins to settle rapidly. Then pass H_2S a little while longer. If the H_2S has been passed through too acid a solution of molybdenum, with the resulting partial precipitation giving a blue filtrate, the best thing to do is to begin over again, giving the proper attention to these details. The molybdenum can be completely precipitated in a half hour's time if the conditions as here given are observed: using a rapid stream of H_2S. Filter and wash this sulphide in the same manner as given for the molybdenum sulphide gotten from filtrate (B), i.e., using a wash consisting of 500 c.c. of water acidulated with a few drops of 1 : 1 HCl and saturated with H_2S. Give the filter sixty washings.

Tungsten Residue (on Filter from (A)).—Burn off in platinum at a low temperature; then fuse with 10 grams Na_2CO_3. Cool; place in No. 5 porcelain dishes; add 150 c.c. water and heat to dissolve the melt. Rinse crucibles and covers with water; add a little pulp; filter through double 9 cm. papers, catching filtrates in clean 400 c.c. beakers. Wash thirty times with water, getting filtrate (B).

Filtrate (B).—Add 2 grams tartaric acid crystals to filtrate (B) and three drops of methyl orange solution; while stirring, add 1 : 1 HCl carefully until solution just turns cherry red. Pass a brisk stream of H_2S through filtrates (A) and (B) until precipitates settle out well—usually requires at least thirty minutes. Add a little paper pulp to each, then proceed to filter (B) through a double 11 cm. filter, catching filtrate in a 1000 c.c. beaker. The filtrate (A) which has already been saturated with H_2S in nearly neutral condition, as described in the first part of the scheme, is poured through the same filter, thus combining the main molybdenum sulphide in (A) with the small amount of the sulphide obtained from (B). The sulphide on the sides of the beakers is removed with a rubber-tipped glass rod. The precipitate is washed with water acidulated with a few drops of HCl to 500 c.c. The water is saturated with H_2S and used cold. Wash the sulphide fifty or sixty times. Ferricyanide of potassium may be used to show freedom from iron. Dry the papers containing the residue at 105° C. for thirty minutes; then roast in porcelain crucible of 40 c.c. capacity at 500° to 550° C. until papers are completely consumed and residues are oxidized to MoO_3. Place in desiccator; let cool about fifteen minutes; then weigh.

Transfer contents of porcelain crucible to clean 150 c.c. beakers, using a camel's-hair brush to remove adhering particles. To each beaker add 40 c.c. filtered ammonia (1 : 1). Heat moderately until white particles are in solution (do not boil too long, because of danger of expelling NH_3, thereby causing deposition of MoO_3).

Filter through double 7 cm. paper, using a small amount of paper pulp in apex of filter. Wash forty times with ammonia water (15 c.c. ammonia 0.90 sp. gr. to 500 c.c. water). Place paper in the same porcelain crucible; burn off as before; cool and weigh. Loss in weight $= MoO_3$, which contains 66.66 per cent $Mo = \frac{2}{3}$.

$$\frac{MoO_3 \times 100 \times 2}{3 \times \text{weight taken for analysis}} = \text{per cent Mo in sample.}$$

THE DETERMINATION OF TUNGSTEN IN THE PRESENCE OF MUCH MOLYBDENUM

Proceed as for molybdenum in high-speed steel as given on page 156, getting filtrate (A). Add 30 c.c. of cinchonine solution (see page 131) to (A). Let stand one hour. If any precipitate forms filter it off at once, washing it with cinchonine water. If (A) is allowed to stand any great length of time some of the molybdenum may separate out with the small amount of tungsten that may be thrown down in (A) by the cinchonine. The small precipitate of tungsten cinchonate that may be gotten from (A) is burned off with the main tungsten residue that remained behind when filtrate (A) was first obtained.

This platinum crucible will now contain the total tungsten contaminated with a little molybdenum. The residue in the platinum crucible is weighed; evaporated with 5 drops of 1 : 3 sulphuric acid and 15 c.c. of HF to dryness. Ignited at the lowest red heat; weighed again. The loss of weight is the silica, which is calculated to silicon by the factor 0.4693.

The silica-free weight equals the main WO_3 plus a little MoO_3 and Fe_2O_3. The silica-free residue is fused with 20 grams of sodium carbonate at a bright red until the fusion is clear and there are no more bubbles arising in the melt. This melt is dissolved out in platinum and any iron oxide is filtered out; washed free of sodium salts; ignited in the same crucible in which the fusion was made and weighed again. This residue should not melt down, but remain as small brown flake. The weight is deducted from the silica-free weight last obtained. This leaves the weight of the WO_3 plus MoO_3. This small amount of MoO_3 is corrected for as follows: The filtrate from the iron oxide is treated with 4 grams of tartaric acid to hold back the tungsten; then made just pink with HCl, using methyl orange as an indicator. The small amount of MoO_3 present is then precipitated out with H_2S, adding a few c.c. more of HCl if necessary to break up the red solution of molybdenum sulphide. The molybdenum sulphide is filtered out; washed thoroughly with H_2S water; ignited at a lowest red heat; weighed and deducted from the weight of WoO_3 plus a little MoO_3. The remainder is the pure WoO_3, which is multiplied by the factor 79.31 and divided by the weight of sample taken to get the percentage of W in the sample.

RAPID METHOD FOR STEELS NOT CONTAINING TUNGSTEN.

Gravimetric by Weighing as MoO_3

Weigh three grams into a 250 c.c. dish, dissolve in 50 c.c. H_2SO_4 (1 : 3) on stove, add 15 c.c. HNO_3 (1.20 sp. gr.) cautiously. Remove and rinse off the lid. Evaporate to fumes. Cover, add 15 c.c. HCl (1 : 1) and 100 c.c. distilled water. Heat until all sulphate is dissolved.

Transfer the contents of dish to 600 c.c. beaker. If considerable silica is seen floating around in test, filter it out and wash it fifteen times with dilute HCl. Add ammonia (1 : 3) until faint cloud of precipitate of iron hydroxide persists; then clear with a few drops HCl; then add an excess of 5 c.c. 1 : 1 HCl. Volume 300 c.c. at this stage.

Pass a rapid stream of H_2S through solution until precipitate settles out well in bottom of beaker. Filter on double 11 cm. papers and wash fifty times with H_2S wash containing a few drops of HCl. Burn off in a 40 c.c. porcelain crucible at 500° to 550° C. Cool; weigh.

Extract in usual manner with filtered ammonia (1 : 1); filter through 11 cm. paper (using pulp); and wash fifteen times with ammonia wash (50 c.c. ammonia (1 : 1) diluted to 300 c.c. with water). Burn off in original crucible; cool; weigh.

$$\frac{\text{Loss in wt.}\times 2\times 100}{3\times 3}=\text{per cent Mo in sample.}$$

Time required to complete determination, one hour forty-five minutes to two hours.

3 grams

$$\begin{array}{r} 23.6290 \\ 23.5910 \\ \hline .0380 \end{array}$$

$$\frac{038\times2\times100}{3\times3} = .844 \text{ per cent Mo.}$$

Weigh 500 mg. into a No. 5 porcelain dish. Dissolve in 50 c.c. HCl (1 : 1); add small additions of $KClO_3$ crystals until solution and residue, if any, are fully oxidized. The solution should become very much darker in color and the tungsten residue in high-speed steel should now be canary yellow.

Boil until the solution smells no longer of chlorine fumes; filter off and discard any residue present. With the solution in the original dish, add KOH solution, while stirring until blue to litmus, then a few c.c. in excess. Bring to a boil; filter through double 12.5 cm. papers into a clean 10×1 inch test tube. Discard the precipitate. (KOH → solution in water, one part KOH to one part water.)

Using a similar test tube, divide this filtrate into two equal portions, so as to have a duplicate handy in case of mishap later. To the solution in one of the tubes, add conc. HCl, in small quantities, shaking to mix after each addition until the test is distinctly acid. If salts deposit in bottom of tube, add a few c.c. of water and shake to redissolve. Add a few particles of c.p. granulated tin, place over a flame and bring just to a boil. Do not continue to boil, as by so doing the delicacy of the test is greatly impaired and at times destroyed entirely. Cool to room temperature; then add 5 c.c. KCNS solution (5 grams KCNS dissolved in 120 c.c. water).

Water-white solution	no trace of molybdenum
Yellowish tinge	0.1 per cent or less
Slight to good orange	up to 0.5 per cent
Deep orange to red	0.5 per cent to 1 per cent
Very dark red......	over 1 per cent.

VOLUMETRIC DETERMINATION OF MOLYBDENUM IN STEEL

After weighing the molybdenum as oxide, the results so obtained can be checked as follows: Fuse the oxide with 5 grams of carbonate of soda. Dissolve the melt in about 50 c.c. of water in a dish. Filter the solution on a 7 cm. filter. Wash the latter thoroughly with sodium carbonate water. Evaporate the filtrate and washings to 50 c.c. Acidulate with 1 : 3 sulphuric acid, adding an excess of 100 c.c. Next add 1 c.c. of 1 : 1 hydrochloric acid after acidulation with sulphuric acid.

Place in the beaker a square inch of 1.7 mm. ($\frac{1}{16}$ inch thick) aluminum foil with its corners bent at right angles. Heat the solution so as to maintain rapid action between the foil and the acid. In a half hour the reduction is *usually* complete.

Titrate with potassium permanganate standard until three drops of the latter render the solution a distinct pink, in the cold, for one minute. Remove the foil before beginning the titration, rinsing it with cold water. Heat a similar piece of foil for a half hour in a solution containing 5 grams of sodium carbonate acidulated with 120 c.c. 1 : 3 sulphuric acid. Add also 1 c.c. of 1 : 1 hydrochloric acid after acidulating with sulphuric acid. Titrate the blank exactly as given for the test. Deduct the c.c. of permanganate used by the blank from the amount required to oxidize the test, and multiply the remainder by 0.001925 to obtain the weight of molybdenum present in the sample. The permanganate standard is prepared by dissolving 1.86 grams of the salt in water and diluting the solution to 1 liter. Its value in metallic iron multiplied by 0.88163 equals its value in MoO_3. This method possesses no advantage over the ignition of the sulphide to oxide and weighing as such.

WEIGHING OF THE MOLYBDENUM AS LEAD MOLYBDATE

After weighing as oxide, fuse the latter with 5 grams of sodium carbonate. Dissolve the melt in water. Filter it, washing thoroughly with sodium carbonate water. To the filtrate and washings add two or three drops of methyl orange. Now titrate the solution until it turns pink with 1 : 1 HCl. Add 1 c.c. in excess. Heat the solution to almost boiling. Add 30 c.c. of a filtered saturated solution of lead acetate in this manner: First add 20 c.c. and permit the precipitate to settle somewhat; then pour in the remaining 10 c.c., noting if there seems to be a further formation of the white precipitate. If more forms, add an additional 10 c.c., or 40 c.c. in all. Now add 50 c.c. of a solution of ammonium acetate. Stir the mixture thoroughly and allow the lead molybdate to settle for two hours. It is filtered, washed with hot water, and ignited at a low red heat until white. It is weighed and the weight multiplied by 0.2614 to reduce the weight to metallic molybdenum. Test the filtrate and washings with 10 c.c. of the lead acetate solution, and note if a further precipitation occurs in the course of an hour or two. This is a satisfactory method, as a check. The ammonium acetate solution is prepared by dissolving 500 grams of the crystals in 1000 c.c. of water.

DETERMINATION OF MOLYBDENUM IN MOLYBDENITE ORES

By Direct Solution in Acids

Weigh 0.2 or 0.3 gram finely ground sample (200 mesh) that has been dried for one hour at 105° C. into 250 c.c. beakers. Add 10 c.c. HNO_3 conc. plus 10 c.c. H_2SO_4 conc. and heat on stove until heavy fumes of sulphuric acid are given off. Cool; add 150 c.c. water; heat to get all the residue in solution as far as possible; make just ammoniacal and then add 10 c.c. excess. Filter; wash with 1 : 20 ammonia; wash forty times and burn off at lowest red heat so as not to volatilize any molybdic acid.

Filtrate and washings from this first silicious and ferric hydroxide precipitate are made slightly acid with H_2SO_4 (1 : 3), and then slightly ammoniacal, using methyl orange as an indicator. Pass H_2S through the solution for one-half hour on graphite bath at low heat; this gives a red solution of molybdenum sulphide; then add 15 c.c. H_2SO_4 (1 : 3) slowly so as not to cause contents of beaker to effervesce over the top and continue to pass gas for one-half hour more. This will completely precipitate all molybdenum sulphide; and the supernatant liquid, after precipitate has settled, should be colorless.

The Separation of Bismuth.—The making of the ammonia precipitation given in the first paragraph is very important as

Brearley and Ibbotson suggested the use of ammonium acetate at this stage.

it prevents the interference of bismuth which is sometimes present to the extent of several per cent. If it is not removed at this stage it will be precipitated with the molybdenum and counted as such at the end of the analysis. This ammonia precipitate will contain all of the silica, bismuth, iron, zinc, alumina, and also all of the arsenic, if there be enough iron present to carry out the arsenic. Also all of the phosphorus.

This bismuth, iron, silica, etc., precipitate is burned off at the lowest possible red heat in a platinum crucible and then fused with 10 grams of sodium carbonate at a bright red heat until the fusion is quiet. The melt is dissolved out in water and filtered; the water-insoluble is washed thoroughly with water containing 5 grams of soda ash to 500 c.c. of water, giving it sixty washings. The residue on the filter will contain all of the bismuth, zinc, etc., and the filtrate and washings will contain the small portion of the Mo that may have been contained in the ammonia precipitate of Bi, etc. Acidulate this filtrate with an excess of sulphuric acid, or about 40 c.c. of 1 : 1 of the acid. Heat to boil off the CO_2. Make slightly ammoniacal. Add 5 c.c. excess ammonia; filter; wash with ammonia wash thirty times and saturate with H_2S as before in a slightly ammoniacal solution for one-half hour longer with H_2S, giving a red coloration. Then add 15 c.c. H_2SO_4 (1 : 3) and continue to saturate for one-half hour longer with H_2S when Mo will precipitate.

Filter this last precipitate through a 15 cm. filter paper, using no pulp, and wash forty times with H_2S wash containing three drops HCl. Then filter the main precipitate of molybdenum sulphide through the same paper and wash sixty times with H_2S wash. The filtering of the small molybdenum precipitate first, washing the filter thoroughly, and then following up with main molybdenum sulphide, eliminates the chance of error due to any sodium salts being retained in the paper or precipitate.

Burn off combined sulphides in platinum crucible at the lowest red heat and weigh. Extract with ammonia (20 c.c. 1 : 1) at low heat on graphite bath for one hour. Filter; wash sixty times with NH_4OH wash (1 : 1); burn off and weigh. The difference in first and second weights being the molybdic acid content plus any copper present.

The presence of copper will be indicated by a blue color in the ammonia filtrate. Any copper thus noted will be titrated with KCN solution, calculated to oxide, and deducted from the molybdic acid content. The remainder should be the weight of the pure molybdic acid content of the ore and can be calculated to MoS_2 by dividing by 0.9.

The Determination of Molybdenum in Molybdenite Ore and Molybdenum Oxide by Fusion

Fuse 0.500 gram of the finely ground ore in a mixture of 10 grams of sodium carbonate and 0.100 gram of potassium nitrate in a platinum crucible. Dissolve the fusion in distilled water. Filter out any insoluble matter; wash the water-insoluble substance with sodium carbonate water (5 grams dissolved in 500 c.c. of water) about thirty times.

Burn off the insoluble in the platinum crucible at the lowest red heat and fuse it again as before, using one-half as much of the fusion mixture. Dissolve out the fusion; filter; wash as before; combine the two filtrates and washings, or if the volumes of the latter are large treat them as follows, separately: Add 2 grams of tartaric acid to the filtrates and washings and stir until the crystals are dissolved. Then make slightly acid with dilute H_2SO_4; and heat for one-half hour to drive off most of the CO_2. Make slightly ammoniacal and add a few drops of methyl orange; add dilute sulphuric acid, a few drops at a time, until a pink color appears. Now pass H_2S through the faintly acid solution for a half hour. The solution will now be a deep blood red and not much molybdenum sulphide will be precipitated. To precipitate the molybdenum now add 5 c.c. of 1 : 3 H_2SO_4 and pass H_2S for another half hour. This should completely precipitate the molybdenum as sulphide, unless the supernatant is still red, in that case add 1 or 2 c.c. more acid and again pass H_2S.

Filter off the molybdenum sulphide and wash it fifty times with H_2S water. Ignite it at the lowest red heat after first smoking off the more volatile part of the filter paper. Continue the heating until the residue is white. Weigh it, and extract it with 1 : 1 ammonia until all but some flocculent matter is dissolved. Filter out the insoluble matter; wash it with ammonia wash; burn it off in the same porcelain crucible in the same way as the main molybdenum; weigh it; and deduct its weight from the first weight of the molybdenum trioxide. Calculate the loss of weight to MoS_2 by the factor 1.1111 or to metal by use of the factor 0.6666. If the residue insoluble in ammonia is more than a milligram or two, transfer it to a platinum crucible and fuse it with twenty times its weight of sodium carbonate and put it through all of the foregoing method to recover any molybdenum that may still be retained in this residue. That is, filter out the water-insoluble from this fusion; wash it with sodium carbonate wash; add a gram of citric acid to hold back the tungsten if any be present; make the filtrate and washings just pink with acid, using methyl orange to give the pink reaction; pass H_2S to saturation; filter out any molybdenum sulphide; wash it; ignite it; weigh it; extract it with ammonia to guard against bismuth; call the loss of weight MoO_3 and add it to the first main loss of weight getting the total MoO_3. Correct this total for CuO as already mentioned in the method by direct solution in acids. (See page 161.)

MANGANESE BY FUSION IN FERRO-MOLYBDENUM AND MOLYBDENUM POWDER

In case the metal, ferro or ore does not dissolve readily in the mixed acids, 0.5 gram of the finely powdered sample is oxidized at a low heat in a platinum crucible with continued stirring and then fused with 10 grams of sodium carbonate. Dissolve the melt in water in a casserole; remove the crucible and acidulate the leached fusion with 50 c.c. of 1 : 1 HCl; clean the crucible with some of the acid and add the cleanings to the main solution. Add also 20 c.c. of conc. H_2SO_4 and evaporate to heavy fumes; cool; add 50 c.c. of water and 50 c.c. of 1.20 nitric acid; boil five minutes; filter into a 250 c.c. volumetric flask; wash thirty times with water and dilute the filtrate and washings to the 250 c.c. mark; mix well; pipette off 50 c.c. into a 10-inch test tube and finish the manganese as in steel by boiling with specially prepared lead peroxide. (See page 338.)

ARSENIC IN FERRO-MOLYBDENUM AND MOLYBDENUM POWDER

Weigh 5 grams of the finely ground ore or metal into a 300 c.c. beaker. Digest on graphite bath with a mixture of 15 c.c. conc.

HNO_3 and 10 c.c. of conc. H_2SO_4 until all action is over; remove the cover from the beaker and evaporate to heavy fumes; repeat this acid treatment until all sulphide or metal is dissolved or oxidized completely.

Cool; add 60 c.c. water; heat for one hour and filter; wash the filter about thirty times with water; make the filtrate and washings ammoniacal to precipitate the iron, Al, and As (at least twenty times as much iron as arsenic must be present, or a weighed amount of iron to that extent should be added). Filter after heating awhile. The filtrate and washings from the iron and arsenic will contain the bulk of the copper and Mo. Dissolve the iron off the filter with cold 1 : 1 HCl; wash the filter well with water; reprecipitate the Fe, As, etc., again as before with ammonia; filter and wash the filter. Repeat these operations at least four times to insure the complete removal of the Mo and Cu from the iron, arsenic and aluminium. Again, redissolve the iron and arsenic as before; wash the filter thoroughly. Evaporate the filtrate and washings containing the iron and arsenic to 100 c.c.; cool; add 200 c.c. of conc. HCl and precipitate the arsenic by passing H_2S through this strongly acid solution for three hours *in the cold* to insure the arsenic precipitating as arsenic pentasulphide. Let the saturated solution settle overnight as small amounts of arsenic separate very slowly from strongly acid solutions. Filter the arsenic pentasulphide mixed with more or less free sulphur, on paper filter; wash thoroughly free from iron with H_2S water containing a few drops of HCl. Purify the pentasulphide from the free sulphur as given in the determination of arsenic in tungsten ores. See page 111. Then weigh as As_2S_5 as described.

Copper.—The three or four ammoniacal filtrates from the arsenic, iron, aluminum precipitations are made acid with some conc. nitric acid and the copper is precipitated therefrom by potassium ferricyanide as in steel and let stand overnight to permit a thorough separation of the copper ferricyanide. The copper precipitate is then filtered off; washed with ferricyanide wash; the paper is burned off in a porcelain crucible; the ash is dissolved with 10 c.c. 1 : 1 HCl; filtered; washed with water; the filtrate and washings are precipitated with H_2S for an hour. Finish for copper as in steel by KCN titration.

DETERMINATION OF MOLYBDENUM IN THE PRESENCE OF ARSENIC

No. 1, 30 mg. Fe; 10 mg As_2O_3; 1994 mg MoO_3 added.
Recovered 2000 gram MoO_3
No. 2, 30 mg. Fe; 20 mg. As_2O_3, 1994 mg MoO_3 added.
Recovered 1990 gram MoO_3.
No. 3, 30 mg. Fe; 30 mg As_2O_3; 1994 mg. MoO_3 added.
Recovered 2000 gram MoO_3
No. 4, 30 mg Fe, 40 mg As_2O_3; 1994 mg MoO_3 added.
Recovered 2000 gram MoO_3
No 5, 30 mg Fe; 50 mg As_2O_3; 1994 mg MoO_3 added.
Recovered 1992 gram MoO_3.
No 6, 30 mg Fe; No arsenic; 1994 mg MoO_3 added.
Recovered 2006 gram MoO_3.

DETERMINATION OF MOLYBDENUM IN THE PRESENCE OF VANADIUM

No. 1 contained 200 mg MoO_3, 30 mg Fe, 50 mg. V_2O_5
No. 2 contained 200 mg MoO_3, 30 mg. Fe, 150 mg. V_2O_5
No 3 contained 200 mg MoO_3, 30 mg Fe, 100 mg V_2O_5
No. 4 contained 200 mg MoO_3, 30 mg Fe, no V_2O_5

MoO_3 RECOVERIES

No 1,	2000 gram recovered	1995 gram added
No 2,	1990 gram recovered	1995 gram added
No 3,	1995 gram recovered	1995 gram added
No. 4,	.1995 gram recovered	1995 gram added

The V_2O_5 range ran from an amount equal to 5 per cent up to 15 per cent on a gram sample and on the 15 per cent V_2O_5 the recovery was as good as on the sample containing no percentage of V_2O_5. Some of the V_2O_5 was found in the filtrate when the molybdenum sulphide was filtered off and part of it was found in the residue from the ammonia extraction of the MoO_3. Used 5 grams of tartaric acid in each precipitation of the sulphide and made the precipitation in an ammoniacal solution; completed the precipitation of the sulphide with addition of 20 c.c. 1 : 3 H_2SO_4.

The carbon and manganese can be determined as in tungsten powder.

ANALYSIS FOUND

	Per Cent		Per Cent
Carbon	1 84	Tungsten	10 02
Manganese	0 32	Molybdenum	42 66
Phosphorus	0 086	Iron	42 12
Silicon	1 85	Sulphur	0 14

Analysis of Wulfenite Ore

Weigh 1.0 to 1.5 grams of finely ground sample (200 mesh) that has been dried for one hour at 105° C. into porcelain casseroles (250 c.c. capacity). Add 50 c.c. HNO_3 (conc.) plus 50 c.c. HCl (conc.); heat for four hours at low heat; then remove covers and take to dryness.

Lead.—Take up with 50 c.c. HCl (conc.), digesting with chlorate of sodium four hours, adding one-half gram chlorate every half hour. Remove from heat just after last addition of chlorate and filter hot solution through 11 cm. papers. Wash sixty times with HCl wash (1 : 20). If the solution is perfect the residue left on the paper will be silicic acid. The solution must not be too dilute and should contain active chlorine from the last chlorating and much free HCl to keep the lead from precipitating as chloride. Burn the filter paper in a platinum crucible at the lowest possible heat until white. Weigh. Evaporate with HF and a few drops of H_2SO_4 to remove silica; ignite the dry residue to the lowest red heat and weigh again. The loss of weight is calculated to percentage of silica.

Note if this residue is pure white. If it is yellow, tungsten may be present. Fuse residue with sodium carbonate (10 grams) and dissolve with HCl (1 : 1). Add this solution to first filtrate plus 20 c.c. H_2SO_4 (conc.) and evaporate to fumes. Cool; add 50 c.c. alcohol plus 150 c.c. water; stir and let settle overnight to precipitate lead sulphate. Filter same; wash sixty times with sulphuric acid wash (1 : 40) and evaporate filtrate to fumes again to obtain any lead still in solution. Filter out this remaining lead sulphate; wash as before.

Combine both papers containing lead sulphate; burn at low heat in weighed porcelain crucible; add three drops HNO_3

(conc.) to oxidize any lead that has been reduced and ignite at low heat to drive off all excess nitric acid. Add three drops H_2SO_4 (conc.); ignite again at low heat to drive off all excess sulphuric acid and weigh; the final weight of the $PbSO_4$ multiplied by factor 0.736 equals lead oxide content of ore.

The filtrate from second lead precipitate is made slightly ammoniacal to precipitate all iron and aluminum present. Filter; wash forty times with NH_4OH wash (1 : 10) and burn off paper in platinum crucible. Precipitate the main molybdenum in the filtrate from the iron and aluminum as in molybdenite ore. Fuse oxide of iron and aluminum in platinum crucible with 10 grams sodium carbonate. Dissolve fusion in 150 c.c. water plus 20 c.c. H_2SO_4 and boil off CO_2. Make ammoniacal; filter off iron and aluminum and precipitate the remaining molybdenum that may have been carried out with the iron, etc., as in molybdenite ore.

Molybdenum.—Combine the two molybdenum sulphide precipitates obtained as described in the foregoing and finish for MoO_3 as in molybdenite ore analysis.

Carbon Dioxide.—Some wulfenites contain considerable lead carbonate. To determine the CO_2, the powdered substance is placed in a carbon combustion furnace and ignited at a red heat for thirty minutes in a stream of oxygen, getting the CO_2 as in steel. (See analysis found in a sample of wulfenite No. 1, given below)

Sulphur can be gotten by the hot tube method (see page 122).

Copper will be found with the MoO_3 and gotten as a correction as in molybdenite analysis.

	Wulfenite No 1	Wulfenite No 2	Wulfenite No 3.
	Per Cent	Per Cent	Per Cent.
PbO	70 27	59 26	61 20
SiO_2	5 05		3 12
Fe_2O_3		.	4 90
Al_2O_3	4 66	6 94	1 05
CO_2	12 20	.	4 24
MoO_3	7 82	22 62	18 81
V_2O_5			1 00
CuO			0 58
P		....	0 137

RESULTS OBTAINED BY THE METHOD ON KNOWN MIXTURES

MoO_3 Added	MoO_3 Found	Lead Added	Lead Found.
Per Cent	Per Cent	Per Cent	Per Cent
0.0546	0.557	0.1009	0.102
0.1092	0.108	0.198	0.196
0.2980	0.2956	0.299	0.300
		0.398	0.397

Tungsten.—In the foregoing scheme any tungsten present would be found with the lead sulphate.

CHAPTER V

PART IV

DETERMINATION OF TIN, BISMUTH AND ARSENIC IN PLAIN AND ALLOY STEELS

DISSOLVE 2 grams of drillings by heating them in a No. 5 porcelain dish on the water bath. After action with HCl is over begin to further attack the steel, if it contains large quantities of chromium and tungsten, by additions of potassium chlorate, 0.500 gram at a time at intervals of thirty minutes until the insoluble residue is bright yellow if tungsten be present. Heat until all smell of chlorine is gone. The sample is usually well decomposed when the amount of chlorate added equals about 2 grams. Now add 50 c.c. of water; heat for a half hour; filter out the insoluble residue and wash the same free of iron test with dilute HCl.

The filtrate and washings are made nearly neutral with ammonia and 20 c.c. of cinchonine solution are added, if the steel contains tungsten, to remove the last traces of the latter. The solution is allowed to stand overnight to make sure that all traces of tungsten are separated. The tungsten is then filtered out, and the filter is washed with cinchonine water as in the determination of tungsten. Any traces of tungsten remaining behind are very likely to contaminate the tin sulphide, obtained later. (This cinchonine solution is made by dissolving 50 grams of the latter alkaloid in 200 c.c. conc. HCl and 800 c.c. of water.)

The filtrate and washings from the cinchonine precipitation are diluted to 400 c.c. and hydrogen sulphide is passed until the mixture of sulphur and sulphides settle well in the hot solution. The sulphides are filtered off and washed with hydrogen sulphide water until free of ferrous iron test to ferricyanide of potassium. This requires fifty washings. Two drops of 1 : 1 HCl are put in 500 c.c. of this wash.

Burn off the mixture of sulphides at a very low red heat in a weighed porcelain crucible. The residue in the crucible may contain small amounts of oxides of copper, molybdenum, bismuth, iron and silicon besides the oxides of tin. The oxides are heated at a red heat for a half hour after the paper is all burned away. The total weight of the oxides is obtained and then the oxides are extracted with 20 c.c. of conc. ammonia to remove the molybdenum. The residue insoluble in ammonia is filtered off; washed with ammonia water; burned off as before; and is then heated with 1 : 1 HCl to remove the small amount of iron, copper and bismuth that may be present. Again the residue insoluble in the HCl is filtered off; washed, and weighed. This weight represents the tin oxide together with a little silica. To remove the silica the residue, after being weighed free of the iron, bismuth and copper, is transferred to a platinum crucible, moistened with 5 drops of the conc. H_2SO_4 and evaporated to dryness with 5 c.c. of HFl to remove the silica. The crucible is then heated to redness again, cooled and weighed. The weight so obtained is calculated to metallic tin by multiplying by the factor 0.7876. A first-class steel will not show by this method much over 0.050 per cent Sn. The author has repeatedly had the method tested by adding known amounts of tin to alloy steels; and has recovered the amounts added within a fraction of a milligram. It must be remembered, in this connection, that chloride of tin is volatile; for this reason the author never heats the samples much above the water bath temperature during the decomposition with hydrochloric acid and chlorate.

In case it is desired to determine both tin and bismuth, it is better to separate these two elements, as given under the determination of Bi and Sn in tungsten powder, when much tin and bismuth are present, page 95, by the use of yellow ammonium sulphide and flowers of sulphur.

ARSENIC IN STEEL

Dissolve the steel, 5 grams, exactly as for tungsten in high-speed steel (see page 171), using a mixture of equal parts of conc. HNO_3 and HCl. Continue to attack the steel in this way until the tungsten, if any be present, is a clear bright yellow. Evaporate to *moist* dryness, only, with additions of HCl until all of the conc. nitric acid has been removed. Finish the arsenic in the HCl solution as given in tungsten ores. Weigh the arsenic as As_2S_5.

CHAPTER VI

PART I

ANALYSIS OF FERRO-CHROME, CHROME ORE AND CARBONLESS CHROME

FERRO-CHROME and carbonless chrome usually dissolve completely in 1 : 3 sulphuric acid. The ferro should be ground as fine as possible. Carbonless chrome dissolves readily without grinding to any especial degree.

When a residue of a gritty or metallic nature remains after digestion with the dilute acid, it is filtered out, washed twenty times with 1 : 10 sulphuric acid, roasted, fused with twenty times its weight of sodium carbonate plus a fifth of its weight of potassium nitrate. The fusion is dissolved in water in a platinum dish, or porcelain one, and then poured into the main solution.

* Dissolve from 0.3 to 0.4 gram of sample in 30 c.c. 1 : 3 sulphuric acid as described, fusing the residue if there be any. Add 60 c.c. 1.20 nitric acid, and treat exactly as stated for determination of vanadium in ferro-vanadium until the filtering through asbestos or a porous crucible to remove the excess of manganese oxide has been accomplished. To the cold filtrate add from 1 to 2 c.c. of the ferricyanide indicator. Add also 50 c.c. of 1 : 3 sulphuric acid. Titrate at once with a standard solution of ferrous ammonium sulphate of double the strength of that used for vanadium work. When 3 drops of this standard produce a darkening of the green to a blue, after the entire disappearance of all red or yellow tints, the end-point is reached.

Standardization and Calculations.—Dissolve 39.163 grams of ferrous ammonium sulphate in water; add 50 c.c. of 1 : 3 sulphuric acid; and dilute to 1 liter for standard. To standardize the ferrous ammonium sulphate weigh into a 5 ounce beaker 0.500 gram of recrystallized c.p. potassium dichromate. Dissolve these crystals in a small quantity of water. Add to the water solution sulphurous acid until the chromate is entirely reduced to a dark green and smells distinctly of SO_2. Then transfer this green solution to a 600 c.c. beaker containing about as much steel, free from chromium, as there is supposed to be iron in the ferro-chromium. For example, if the ferro is supposed to contain 60 per cent chromium, use 0.160 gram of steel. The steel is dissolved in 30 c.c. 1 : 3 sulphuric acid before the reduced chromium solution is added to it. Put this standardizing mixture through all of the analytical operations given for the actual analysis of the ferro-chromium, including the addition of the nitric acid.

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* Use from 0.2 to 0.25 gram if Cr in the ferro is over 50 per cent Cr.

CALCULATIONS

The ferrous ammonium sulphate used by the 0.500 gram $K_2Cr_2O_7$ is, for example, 102.6 c.c. The percentage of chromium in the dichromate is 35.35. Therefore 0.500 × 35.35 ÷ 102.6 = 0.001724, or 1 c.c. of the ferrous ammonium sulphate solution equals 0.001724 gram of chromium.

A check standardization using 0.600 gram of $K_2Cr_2O_7$ gave 1 c.c. equals 0.001713. The average value is 0.001718. Suppose 0.300 gram of a ferro-chromium required 99.9 c.c. of the sulphate standard: 99.9 × 0.001718 ÷ 0.3 = 0.5721, or 57.21 per cent chromium.

CARBON

The total carbon can be obtained quickly by the means of some oxidizing flux in a stream of oxygen. Direct combustions with oxygen alone are very incomplete, at least with temperatures of 950° C. and under. Decarbonize 1 gram of 60-mesh sample, or finer, with 4 grams of red lead, either in the gas or electrically heated furnaces.

SULPHUR AND SILICON

Fuse 1 gram of the finely powdered alloy in an iron crucible with a mixture of 10 grams of Na_2O_2 and 5 grams of Na_2CO_3 for two or three minutes in the manner described under ferro-titanium. (See page 57.) Hold the crucible in the flame with a pair of tongs giving it a moderate rotary motion during the three minutes of quiet fusion.

When the melt is cold, place the crucible on its side in a porcelain dish or casserole. Cover it with water; warm it as little as possible to prevent attacking the glaze of the dish. When the solution is complete, remove the crucible, rinse off its sides into the dish, and rub off and wash into the dish any oxides adhering to its inner walls.

Add an excess of HCl; evaporate dry; take up in water and HCl, heating until all but the silica is in solution; cool; filter out the silica, mixing in some ashless filter pulp to aid filtering and washing; wash free of iron test; smoke off the filter from the silica in a platinum crucible and then raise the heat gradually and finally blast to a constant weight. Call this (A). Evaporate the filtrate and washings from the main silica again to dryness to get out the last traces of silica; take up with water and HCl as before; filter out the small amount of silica; wash it free of iron test with 1 : 40 HCl; and burn it to an ash in the same crucible with (A). The total ash in (A) will now contain the total silica. Ignite it to a constant weight ; evaporate it to fumes with 15 c.c. of HF and 3 c.c. of 1 : 3 H_2SO_4. Raise the heat gradually to a dull red; cool; do not blast; cool and weigh. The loss of weight of (A) multiplied by 49.63 and divided by the weight taken will give the total per cent of silicon in the sample. Deduct the blank before making the calculation. Also if the silicon is high, being several per cents, it should be again evaporated. This time with 7 c.c. of HF and 20 drops of 1 : 3 H_2SO_4; ignite to a dull red and weigh again to make sure all of the silica has been driven off. The residue from this second evaporation is fused with twenty times its weight of Na_2CO_3 mixed with the equal of its weight of niter. Heat slowly to a bright red and keep at this heat for twenty minutes. Dissolve the fusion out in water in a platinum or porcelain dish. Add 1 : 1 HCl to dissolve the fusion if a porcelain dish is used, as the hot alkaline solution will attack the glaze of the dish. Clean the crucible with a little acid; add these cleanings to the solution of the fusion; add an excess of HCl; heat until all is in solution; and add the entire fusion to main filtrate and washings from the second evaporation made to get out the last traces of silicon. This total solution will now contain all of the Cr, Mn, S, Al, P, Cu, Ni and V and can be analyzed for these elements by nearly the same methods as given for ferro-titanium by fusion. However, it is better to get the phosphorus and sulphur only from this solution.

SULPHUR AND PHOSPHORUS

Add a slight excess of ammonia to the solution last mentioned; heat; filter out hydroxides of iron, etc., using two funnels and 15 cm. filter papers as the precipitate will be of large bulk. Wash with water; acidulate the filtrate and washings with HCl; add 10 c.c. excess of 1 : 1 HCl; volume at this stage should be not much over 400 c.c. Too much free HCl prevents the complete precipitation of $BaSO_4$; on the other hand if the solution is too nearly neutral the $BaSO_4$ forms in a state of extremely fine division, settles very poorly, and has a decided tendency to run through the filter paper.

Now add to the hot solution 50 c.c. of a saturated solution of $BaSO_4$ diluted with 100 c.c. of water; stir thoroughly and let settle overnight. Finish the sulphur as in steel by the gravimetric method. The hydroxides of iron, chromium, etc., on the two filter papers contain all of the phosphorus. Dissolve them off the filter papers as far as possible with hot 1 : 1 HCl; wash the papers thoroughly with water. Burn them to an ash; fuse the ash with twenty times its weight of Na_2CO_3 mixed with once its weight of KNO_3. Dissolve out the melt in HCl and add it to the main solution of the hydroxides. Then evaporate the latter to 15 c.c.; add 75 c.c. of conc. HNO_3; heat with the cover on until all action is over; evaporate to 15 c.c. again; repeat the evaporation with conc. nitric, using 50 c.c.

Wash the nitric solution of the hydroxides into a 125 c.c. beaker and evaporate to 25 c c Add 20 c.c. of conc. nitric acid; heat to boiling; remove from the fire and add, at once, 50 c.c. of the faintly ammoniacal solution of ammonium molybdate. Stir rapidly for two or three minutes; filter off the phosphomolybdate as soon as it has settled. Finish as for phosphorus as in steel.

CHROMIUM

Instead of running all of the nitric acid solution of the iron and chromium for phosphorus, it can be divided into two equal parts. One part can be finished for phosphorus and the other half can be diluted to 300 c.c., boiled with $KMnO_4$ and finished by titration with ferrous ammonium sulphate as already described for chromium.

The scheme described on pages 47-48 for the analysis of ferro-titanium calls for the transfer of the solution containing the total Cr, Mn, S, Al, P, Cu, Ni, etc., to a liter flask; dilute to the mark; mix well; repeatedly inverting the stoppered flask. 50 to 100 c.c. of this solution are measured off into evaporating dishes.

MANGANESE

To this 50 and 100 c.c. are then added 10 c.c. of 1 : 1 HCl and then a slight excess of a thick cream of zinc oxide and water to remove the chromium. Chromium interferes seriously with the determination of manganese by lead peroxide method. Filter off the precipitate, consisting of hydroxides of iron and chromium; wash them thoroughly with water. Add to the filtrate and washings about 15 c.c. of 1 : 3 H_2SO_4 and evaporate to thick fumes to remove the HCl.

Add 10 c.c. of water and heat until all sulphate is dissolved; transfer the solution to a 10×1 inch test tube; add 10 c.c. of conc. HNO_3 and finish by boiling with brown lead peroxide; titrate for manganese as in steel with standard sodium arsenite solution. If the manganese is higher than 2 per cent, the sulphate solution should be finished with a larger amount of nitric acid; boiled with more brown lead; and titrated with ferrous ammonium sulphate as described on page 345 for per cents up to 16 per cent Mn.

IRON, ALUMINUM AND MANGANESE BY SOLUTION IN HF AND H_2SO_4

Dissolve 1 gram of the finely powdered alloy in the same way as described for ferro-titanium, in a covered platinum dish in 10 c.c. of HF; warm in a good draught; remove from the heat; add a few drops of conc. nitric acid; when action is over, continue to add the HNO_3 until a total of 5 c.c. has been used; remove the lid; wash the under side of the cover into the dish; add 10 c.c. of conc. H_2SO_4; evaporate to *slightest fumes only* (difference from titanium procedure). If a solution containing chromium is evaporated to thick fumes of SO_3, the chromium becomes very insoluble.

The sulphate of iron (chromium, Al, Mn, etc.) is again gotten into solution by heating it with water and H_2SO_4. It is again evaporated to slight fumes to insure the complete removal of the chlorides. The sulphates are again dissolved by heating with water; the whole is transferred to a liter flask; and diluted to the mark; mixed well by repeatedly inverting the flask. The 500 c.c. portion taken for the Al, Fe is evaporated to 300 c.c. and peroxidized in a beaker by adding Na_2O_2 until slight alkalinity is obtained to litmus paper; 5 grams excess peroxide and 5 grams of Na_2CO_3 are added and the whole is brought to a boil for a few seconds only. The volume at this stage should be about 600 c.c. The iron hydroxide, which still may contain considerable Cr and Al, is filtered off and washed with carbonate water (5 grams dissolved in 500 c.c. of water). The yellow filtrate and washings will contain most of the Al and Cr. The iron hydroxide is dissolved off the filter with hot 1 : 1 HCl. The filter paper is washed thoroughly with 1 : 40 HCl until free of iron test. The filter paper is saved.

The filtrate and washings are again peroxidized as before; the iron hydroxide filtered off and washed. If the filtrate and washings are still yellow, the iron hydroxide must be again dissolved off as before, the filter washed free of iron and saved. The filtrate must be again peroxidized and so on until an alkaline filtrate and washings are obtained free of yellow and on neutralizing to turmeric paper gives only a slight cloud of Al hydroxide or none at all. Where much Cr or Al or both, are present this may require at least three peroxidations.

The filter papers from which the iron hydroxide is dissolved off prior to each peroxidation, are saved, as stated, and burned to an ash at a low heat; weighed. The ash (which may be partly fused already from the small amount of carbonate remaining in it from the washing), is fused with twenty times its weight of Na_2CO_3 and twice its weight of niter for fifteen minutes at a bright red heat; the melt is dissolved out with water; filtered; washed with carbonate water; the filtrate and washings are added to the yellow filtrates from the peroxidations of the iron. However, if this filtrate and washings from the fusion of the ash shows green tints, it contains sodium manganate which must be removed by heating in the filtrate and washings, a few drops of alcohol. The Mn will settle out as a brown precipitate, which is filtered out and washed with carbonate water. This operation should be done before the solution of the fused ash is filtered in the first place.

The residue on the filter from the solution of the fused ash is added to the main iron hydroxide which is left on the filter after the last peroxidation to remove the last traces of the Al and Cr. This iron hydroxide (which is now free of Al and Cr), together with the small residue obtained from the fusion of the several filter paper ashes after the warming of the water solution of the fusion with alcohol, will contain the total iron and manganese in the one-half gram portion of the alloy.

Iron and Manganese.—The last-mentioned chromium-free iron and the small residue of iron and manganese on the filter from the water and alcohol solution of the fused filter ash can now be dissolved off the respective filters with hot 1 : 1 HCl as far as possible. To make sure of dissolving all of the manganese treat the filter papers further with some sulphurous acid water which is most effective in dissolving manganese. Then wash thoroughly with 1 : 40 HCl and dilute sulphurous acid water. The filtrate and washings are then evaporated to thick fumes with 40 c.c. of 1 : 3 H_2SO_4. Cool; heat with water and 10 c.c. more of H_2SO_4 until all sulphates are dissolved; cool; transfer to a 500 c.c. volumetric flask; dilute to the mark; mix well; take one-half and put through the reductor for iron, as in iron ore, and finish the other part in 50 and 100 c.c. portions for manganese as in steel, proceeding according to whether the manganese is over or under 2 per cent Mn.

Aluminum.—As just described, the 500 c.c. of the iron-chromium aluminum solution are peroxidized until a filtrate and washings are obtained that are free from yellow tint and do not give even a slight cloudiness when made just neutral to turmeric paper and still slightly acid to litmus paper.

The several alkaline filtrates and washings together with the small filtrate from the water solution of the sodium carbonate fusion of the filter ashes (the water solution in which the few drops of alcohol were heated to precipitate any manganate) will contain all of the Cr and Al and V (if any is present) in one-half gram of the alloy.

These filtrates and the small alcoholic filtrate are each in turn neutralized to turmeric with HCl as fast as they are obtained to note the amount of Al being separated at each peroxidation. In this way one can tell whether it is necessary to make another peroxidation or not.

The precipitates of Al hydroxide obtained from the neutralization of these filtrates and washings are combined on one 15 cm. filter, after mixing in with them some ashless filter paper pulp to aid the filtration and washing. Filter on a double filter paper. Wash with ammonium nitrate water (5 grams of the salt dissolved in 500 c.c. of water). The washed Al will contain too much occluded salts for ignition and weighing, therefore it is dissolved off the filter with hot 1 : 1 HCl, pouring the latter back and forth over the paper and pulp several times, stirring up and upsetting the latter to make sure that the acid gets to all parts of it. The paper and pulp is then washed with 1 : 40 HCl and then with water, stirring and upsetting the pulp frequently and permitting each washing to drain off thoroughly before another one is applied.

This filter paper and pulp is saved to burn with the reprecipitated Al. The Al can now be precipitated from the hot filtrate and washings free of occluded salts with slight excess of ammonia. It is boiled two or three minutes, filtered off and washed as before. It is smoked off in a platinum crucible in which the previous filter paper and pulp (from the crude Al solution) has been burned. The carbon-free ash is blasted to a constant weight and weighed as Al_2O_3 plus a little Cr_2O_3 plus a little SiO_2 plus a little P_2O_5 if any of the latter be in the reagents.

The Al_2O_3, etc., after blasting and weighing, is evaporated with 7 c.c. of HF and 4 c.c. of 1 : 3 H_2SO_4; ignited and weighed again as Al_2O_3 plus a little Cr_2O_3 plus what little P_2O_5 is gathered from the reagents. To correct for the two latter impurities fuse the Al_2O_3, etc., with twenty times its weight of Na_2O_3 plus the equal of its weight of niter at a bright red heat for thirty minutes. Dissolve the fusion out in water. Transfer it to a porcelain dish; acidulate it with HCl; heat with the cover on until most of the CO_2 is gone and all is in clear solution; cool; transfer to a 500 c.c. volumetric flask; dilute to the mark; mix well; take 250 c.c. and evaporate it twice to slight fumes with 1 : 3 H_2SO_4; cool it; add water; heat until all is dissolved and finish for Cr as in steel; calculate the Cr so found to Cr_2O_3 by use of the factor

1.4615. Deduct the milligrams of Cr_2O_3 so found from the Al_2O_3, etc. The remaining 250 c.c. are converted to nitrates by evaporating twice to 10 to 15 c.c. with 75 c.c. of conc. nitric acid; transfer to a 150 c.c. beaker. Finish for phosphorus as in steel; multiply the milligrams so found to P_2O_5 by use of the factor 2.2886. Deduct the P_2O_5 obtained from the Al_2O_3, etc., remaining after Cr_2O_3 was deducted. The Al_2O_3 having been freed of SiO_2 by the HF and corrected for Cr_2O_3 and P_2O_5, the remainder of weight is now calculated to Al by use of the factor 0.53033. This product multiplied by 100 and divided by 0.500 will give the percentage of Al in the alloy

Iron and Chromium (Second)

Iron.—The other 500 c.c. portion of the original liter solution of the 1 gram of the alloy by HF and H_2SO_4 and HNO_3 can be divided into two parts—250 c.c. (equal to 0.250 gram of the sample), and put through the reductor and titrated for iron, as Cr does not interfere with this titration with standard $KMnO_4$ except the color effect it may have on the pink end-point.

Chromium.—200 c.c. of the liter solution (equal to 0.200 gram of the sample) can be boiled with an excess of $KMnO_4$; filtered; and the filtrate finished for Cr by titration with standard ferrous ammonium sulphate, back titrating to a slight pink with standard $KMnO_4$ as described on page 17. Or by use of potassium ferricyanide as an internal indicator it can be titrated to a blue end-point with standard ferrous ammonium sulphate, alone, for Cr.

The total Cr can also be obtained by combining all of the yellow filtrates from the Al hydroxides precipitated by neutralizing the alkaline filtrates obtained when the Al is separated from the iron, etc., by peroxidation. Add to the Cr so found the small amount found in the final Al_2O_3.

Method for Soluble Ferro-chromium and Metallic Chromium.—Low silicon ferro-chromium and metallic chromium are of this type. The method answers well for Fe, Mn, Cr, Al, Ni, Cu and Si, but not for P or As.

Method.—Dissolve 1 gram of the finely powdered alloy as far as possible in 40 c.c. of 1 : 3 sulphuric acid. Evaporate to slight fumes of SO_3. Redissolve in water and a little more

H_2SO_4, heating until all sulphate of iron is in solution; filter out the silica; wash it with 1 : 40 H_2SO_4; then with water; evaporate the filtrate and washings again to slight fumes, only. If taken to heavy fumes, the anhydrous chromium sulphate formed is very insoluble. Take up again as before, filtering out the silica that may not have been separated by the first evaporation. Wash free of iron as in the first evaporation. Burn the silicious residues from the two evaporations together; ignite and weigh; evaporate with 15 c.c. of HF plus 10 drops of H_2SO_4; ignite again as before. The loss of weight equals the SiO_2, which, multiplied by 46.96, gives the Si.

The residue in the crucible after the HF evaporation and weighing is fused with twenty times its weight of Na_2CO_3 and the equal of its weight of niter; the melt is dissolved out in water; the crucible is cleaned by warming in it a little 1 : 1 H_2SO_4; the water solution is acidulated with H_2SO_4; heated until all is dissolved and added together with the cleanings of the crucible to the main filtrate from the last evaporation to remove the last of the silica.

The filtrate and washings now contain all of the Cr, Mn, Fe, Al, Cu, Ni, and V in the alloy, and these elements are determined exactly in the same manner as described when the alloy is dissolved in HF plus HNO_3 plus H_2SO_4.

COPPER AND NICKEL

Get 1 to 5 grams of the sample into solution by the HF—HNO_3—H_2SO_4 method or by the method for soluble ferro-chrome; saturate the sulphate solution with H_2S; filter out the copper sulphide; wash it with slightly acidulated H_2S water; finish the copper as in steel. The filtrate and washings from the copper are evaporated to slight fumes, adding a few crystals of $KClO_3$ before the evaporation becomes too concentrated. (Chlorate explodes if heated with concentrated sulphuric acid.) The oxidized sulphate solution can then be finished by precipitating the nickel out with dimethyl, keeping the Cr and Fe from precipitating by use of citric acid. See method for steel. When the sample is gotten into solution by the method for soluble ferro-chrome and metallic chrome, the H_2S should not be passed until the residue from the HF evaporation is fused, dissolved, and put back into the main filtrate from the silica as this residue may contain an appreciable amount of the copper.

Blanks and Check Mixtures.—The operator should without fail run blanks when making any of the determinations described under the Analysis of Ferro-Chromium. The iron can be added in the form of a steel of a known iron content or a standard iron ore. The chromium can be added as recrystallized potassium dichromate; the copper as metallic copper; the nickel as the double sulphate of nickel and ammonium; and the Al as metallic Al. As the latter is very slightly soluble in H_2SO_4, it can be first dissolved in HCl; converted to sulphate by fuming it with H_2SO_4 and then added to the solution of the mixture before evaporating it to dryness to get the silicon blank.

SULPHUR BY EVOLUTION IN A STREAM OF HYDROGEN SATURATED WITH HCl; AT A TEMPERATURE OF ABOUT 950° C.

Place 0.500 gram of the finely powdered sample in a tapered clay combustion tube; fill the cold tube with the H; turn on the electric current; raise the heat gradually to 950° C.; continue to pass the acid hydrogen, catching the H_2S formed in a 10×1 inch test tube filled three-fourths full of ammoniacal cadmium chloride solution. Change absorbing solution every forty-five minutes until a tube is obtained that shows no cadmium sulphide. Finish by titrating with iodine standard as in steel.

CHROMIUM IN CHROME ORE

Fuse 0.6 gram with 8 grams of sodium peroxide in a 45 c.c. porcelain crucible. Keep the fusion molten for five minutes. Three or four melts can be made of chrome ore in a porcelain crucible before the peroxide cuts through.

Place the crucible in a 375 c.c. casserole. Cover with a watch glass. Stand the crucible in the bottom of the casserole. Allow water to flow slowly down the under side of the watch glass and drop into the open crucible. The melt promptly boils up and dissolves in a few moments. Remove the crucible. Boil the water solution, without filtering, for one-half hour to remove all hydrogen peroxide. The excess of peroxide would reduce some of the chromic acid, if allowed to remain, just as soon as the fusion is acidulated with the sulphuric acid. Add 50 c.c. *excess* of 1 : 3 sulphuric acid.

Add 3 c.c. of the ferricyanide indicator to the cold sulphuric acid solution and titrate it as in ferro-chrome, using the same standard. Standardize by fusing 0.340 gram of potassium dichromate in 8 grams of peroxide in a porcelain crucible, and complete the operation as in actual analysis. Multiply the number of milligrams of metallic chromium found by 152 and divide by 104 to obtain the milligrams of chromium oxide in the ore, or

$$Cr \times \frac{19}{13} = Cr_2O_3.$$

As the samples of ferro-chromium and chrome ore are likely to vary somewhat, especially in the case of ferro-chromium, several determinations should be made of the same sample and the results averaged.

Porcelain crucibles are not suitable for fusion of *metals* with sodium peroxide, as great heat is generated, causing the crucible to crack. This is not the case in chrome ore.

INSOLUBLE FERRO-CHROMIUM

Ferro-chrome that is not attacked by acids can be conveniently assayed for chromium as given for chrome ore, but as the porcelain crucible usually cracks during the cooling a new crucible is needed for each fusion.*

Weigh 0.500 † gram of the finely ground ferro and fuse it with 8 grams of sodium peroxide.

THE DETERMINATION OF CHROMIUM IN FERRO-CHROMIUM BY FUSION IN AN IRON CRUCIBLE

Fuse 0.200 gram of the ferro if the chromium is about 65 to 70 per cent in chromium content, or a proportionately larger weight if the chromium content is lower, in a 70 c.c. iron crucible with 8 grams of sodium peroxide. In making the fusion the crucible is held in a pair of tongs and given a moderate swirling motion in the flame of an ordinary Bunsen blast burner. In two minutes the melt should be liquid and after two more minutes the fusion should be perfect. During the fusing it is wise to place the burner in an enameled ware pan as, in case the flux cuts through the crucible, the drops of the red-hot flux will be caught in the pan, instead of being spread far and wide. After cooling the crucible is placed in a 600 c.c. casserole; a lid is placed on the latter and the fusion is dissolved in 150 c.c. of water, which is allowed to flow very slowly down under the watch glass into the open crucible. The water solution of the fusion is boiled for a half hour to remove all hydrogen peroxide; the crucible is removed from the casserole; 150 c.c. of 1 : 3 sulphuric acid are added; and the solution is heated for ten minutes. The iron scales are filtered out on an asbestos plug (see page 298) and the plug is washed with water thoroughly; the filtrate and washings are diluted to 400 c.c. with distilled water; 3 c.c. of indicator are added (5 grams of potassium ferricyanide dissolved in 120 c.c. of water) and the solution is titrated to the first distinct blue with the same standard as given on page 174.

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* Iron crucibles are preferable for this work. Use a 65 c c. crucible. Keeping the lid on, grasp the body of the crucible with the forceps; hold it in the flame of a Bunsen burner until molten. Then give the crucible a slight rotary motion for a period of three or four minutes, or until the entire mass is in a state of homogeneous fusion.

† From 0.2 to 0.25 gram if Cr in the ferro exceeds 50 per cent Cr.

Chrome Ore.—Chrome can also be analyzed as above for chromium, taking 0.500 gram for the analysis; but for the most accurate work the author prefers the method given on page 184, as the fusion in porcelain dissolves in the sulphuric in the most satisfying way, being as clear as a filtered solution except for a few scattering pure white flakes of floating silicic acid. The fusion in porcelain is also desirable for iron determination as the sulphuric acid solution can be reduced at once without separating the chromium and titrated for iron with the standard permanganate solution (see page 443).

Standardization.—For either of the above methods fuse 0.400 or 0.450 gram of recrystallized potassium dichromate in 8 grams of the sodium peroxide and put the same through all of the above operations and titrate the resulting solutions with the permanganate solution to be standardized, calculating the chromium value of the standard in the same manner as given on page 174.

CHAPTER VI

PART II

THE ANALYSIS OF CHROME CEMENT

Ignition Loss.—Heat 1 gram of sample for a half hour in a weighed platinum crucible at a bright heat and weigh the crucible and its contents again and note the loss of weight. Return the crucible to the flame and heat at ten-minute intervals until the loss for ten minutes heating no longer exceeds 0.0002 gram. The total loss of weight is calculated to percentage as the ignition loss.

Silica, Iron and Aluminum Oxides.—Fuse 0.5 gram of sample with 15 grams of potassium acid sulphate ($KHSO_4$) in large platinum crucible, in the manner described on page 56, until a clear solution is obtained. Cool; dissolve in water and hydrochloric acid. Boil; filter off the silica; wash it; finish it as usual getting the loss of weight with HF and a few drops of conc. H_2SO_4. The residue remaining in the crucible after this evaporation and ignition is fused with 4 grams of $KHSO_4$. Dissolve it as in the main fusion, adding the solution to the main filtrate from the silica. This filtrate contains all of the iron and aluminum. The aluminum is separated from the iron by peroxidation with sodium peroxide until a filtrate is obtained that does not show any more precipitate with the HCl than a blank determination. (See page 178.) The iron on the filter from the last filtration together with any that may be adhering to the walls of the peroxidation flask is dissolved in HCl and finished by reduction with stannous chloride as in iron ore. The iron found is calculated to FeO. The aluminum is purified from occluded salts by redissolving it in HCl and reprecipitating it with a slight excess of ammonia. Before filtering off the aluminum it should be boiled for some minutes. It is washed with ammonium nitrate wash, ignited, blasted, cooled and weighed as Al_2O_3 plus a little silica which is removed by evaporation with some HF plus 10 drops of conc. H_2SO_4. Deduct blanks.

Chromic Oxide.—Fuse 0.3 or 0.4 gram of the sample in 8 grams of sodium peroxide in an iron crucible and finish as in chrome ore. (See page 184.)

RESULTS

	Per Cent		Per Cent
Ignition loss	2 34	Silica	3 21
Iron monoxide (FeO)	30 00	Chromic oxide (Cr_2O_3).	40 80
Alumina .	23 20		

Note.—Sodium carbonate fusions are not successful as a method of decomposing the above cement.

CHAPTER VII

PART I

THE DETERMINATION OF LARGE AND SMALL PER CENTS OF ALUMINUM AND ZIRCONIUM BY FIRST REMOVING THE BULK OF THE IRON WITH AMMONIA

ALUMINUM IN PLAIN STEEL

DISSOLVE on a low flame 5 or 10 grams of steel in 50 c.c. 1 : 3 H_2SO_4 diluted with 50 c.c. of water. After action is over filter off the insoluble residue which is mainly carbon and carbides, wash it twenty-five times with dilute H_2SO_4 wash. Call this filtrate and washings (A). The insoluble residue may contain Al, so it must be ashed in a platinum crucible at a low heat; cooled; 6 c.c. of HF plus 6 c.c. of 1 : 3 sulphuric acid added; evaporated to thick fumes of SO_3; cooled; a little water added; heated to dissolve the sulphates and the clear solution is added to (A). Then dilute (A) to 250 c.c. volume with water and add slowly 1 : 1 ammonia with constant stirring until the reddish precipitate changes to a blackish color. *All the aluminum is precipitated with but 3 or 4 per cent of the iron.* Filter aluminum plus a little iron off at once; redissolve it in 50 c.c. hot 1 : 1 HCl, pouring the acid back and forth until all the iron and aluminum are in solution. Wash the filter paper about forty times with dilute HCl water. Peroxidize the filtrate with sodium peroxide until the solution changes red litmus paper to a blue. Add about 5 grams of sodium carbonate; bring it to a boil and filter off the iron. Wash the precipitate about thirty times with water.

If the pulp mixed with the precipitate is washed thoroughly no more aluminum will be left with the iron, otherwise it is necessary to redissolve the iron in hot 1 : 1 HCl and make another peroxidation. To the filtrates add 1 : 1 HCl with constant stirring until turmeric paper does not change even to faintest brown when dipped into the solution, but red litmus paper turns slightly blue when dipped into it. Aluminum is precipitated at this stage. After a few hours, especially when aluminum per cent is low, filter off the precipitate and wash it about forty times with ammonium nitrate, to remove the salts as far as possible. To free the aluminum from all sodium salts the aluminum is redissolved in 50 c.c. hot 1 : 1 HCl. Wash filter forty times with dilute HCl wash. (Wash the filter paper free of chloride with water and save it to burn with the main final precipitate, as aluminum is liable to remain in the filter.)

Precipitate the aluminum by adding 1 : 1 ammonia to the filtrate until faintly ammoniacal. Bring it to a boil and filter off the aluminum hydroxide. Wash it free of chloride with ammonium nitrate. Burn off in a weighed platinum crucible and blast it to a constant weight. Weigh it as Al_2O_3 plus SiO_2. Remove the silica by evaporation with a few drops of 1 : 1 H_2SO_4 and 10 c.c. of HF. The remainder is Al_2O_3. Multiply by 53.033 to calculate to percentage of aluminum.

ALUMINUM RECOVERIES FROM STEEL

Weight of Steel Taken	Aluminum Added	Aluminum Found	Weight of Steel Taken	Aluminum Added	Aluminum Found
15 grams	.010 gram	0102 gram	5 grams	030 gram	030 gram
10	020	0199	5	100	1005
5	050	0508			

Same weights of steel without any aluminum added were put through all of the foregoing operations and the blanks found were deducted from the above five samples. All filter papers from which any precipitates are dissolved off with acid must be washed free of iron and ashed. The ash is always liable to contain some Al. This ash is fused with twenty times its weight of sodium carbonate at a bright red heat; the melt is dissolved out in 1 : 1 HCl; a peroxidation is made of it in a small volume and any aluminum it contains is gotten exactly as in the foregoing, and burned off with the main aluminum before it is evaporated with HF and a little H_2SO_4 to remove the silica.

By the method as given extremely small amounts of Al can be detected and determined with great accuracy.

Test Mixture.—Dissolve a known amount of metallic aluminum in 1 : 1 HCl, fume it with 1 : 3 H_2SO_4, dissolve in water, and 1 : 3 H_2SO_4; and add this Al sulphate to the sulphuric acid solution of a plain carbon steel before it is filtered free of the free carbon and carbide residue. Then put this through all the operations. Any of Al recovery in excess of the amount added, equals the blank to be deducted. Use same weight of plain carbon steel as is used for the Al steel.

NOTE.—All U, V, Cr, Zr, and Ti present come down with the aluminum, and are filtered off with the Al away from the bulk of the iron when the first ammonia precipitation is made. The above method for Al removes everything away from the Al except small contaminations of Cr and V, if these two elements be present in large quantities To correct for traces of Cr and V, the Al_2O_3 plus a little Cr and V oxides can be fused with sodium carbonate and a little niter in a platinum crucible; the fusion dissolved out in water; made acid with HCl and heated until in clear solution in a casserole; converted to sulphates; boiled with a slight excess of $KMnO_4$; filtered through a porous filtering crucible; titrated for V and Cr in the usual way with $KMnO_4$ standard and ferrous-ammonium iron sulphate standard, with ferricyanide as an internal indicator. The V and Cr so found are calculated to V_2O_5 and Cr_2O_3 and deducted. All this is rarely necessary, but should be done if the Al_2O_3 is not fairly white or looks grayish from Cr_2O_3 or golden yellow from V_2O_5.

ALUMINUM AND ZIRCONIUM

Dissolve 4 grams of sample in 50 c.c. of 1 : 3 H_2SO_4 diluted with 50 c.c. of water. After action is over, filter off the insoluble residue which is mainly carbides. Wash the carbides twenty-five times with dilute H_2SO_4 wash. Call this filtrate and washings (A). The insoluble carbides will contain some Al and Zr. Ash these in a platinum crucible at a low red heat. Cool; add 6 c.c. HF plus 6 c.c. of 1 : 3 H_2SO_4; evaporate to thick fumes; cool; add a little water, heat until all sulphates are in solution and add latter to (A). Dilute (A) to about 250 c.c. volume with water and add 1 : 1 ammonia with constant stirring until the first appearance of a black precipitate forms. Add a *few* drops in excess. At this stage all the zirconium and aluminum have been precipitated with a *very small percentage of the iron.* Filter off at once and redissolve precipitate in 50 c.c. of hot 1 : 1 HCl. Wash the paper with dilute HCl wash till it looks perfectly white. Concentrate the filtrate and washings to about 50 c.c. volume and peroxidize with sodium peroxide till the solution is alkaline. This peroxidation is carried out in the following manner; add from a small porcelain spoon about 1 gram at a time of Na_2O_2.

Rinse off spoon into beaker with each addition of the peroxide and stir the solution each time and so on until the solution is alkaline. By this process the volume reaches about 300 c.c. by the time it is alkaline. Then add 5 grams of Na_2CO_3; bring it just to a boil and filter off the iron and zirconium. Wash precipitate with water about twenty-five times. The filtrate contains the aluminum. Redissolve the iron and zirconium in 50 c.c. of hot 1 : 1 HCl and peroxidize again as before to remove the last traces of aluminum.

Add to the filtrate 1 : 1 HCl with constant stirring until turmeric paper does not change even to a faint brown when dipped in the solution, but red litmus paper gives a slight alkaline reaction. Keep cover on while adding the acid. Leave aluminum settle for a few hours and after filtering it off, wash it about forty times with ammonium nitrate wash. Redissolve the aluminum with hot 1 : 1 HCl; wash it with dilute HCl water (wash the papers also with water and burn off with the main precipitate as some aluminum is liable to remain in the papers).

To the filtrate and washings add 1 : 1 ammonia till slightly ammoniacal. Aluminum is precipitated. Now bring it to a boil, filter it off and wash it free of chloride. Burn it off in a weighed platinum crucible to a constant weight. Remove the silicon by evaporation with HF acid and a few drops of 1 : 3 H_2SO_4; again weigh as Al_2O_3. Multiply by 53.033 to calculate to percentage of aluminum.

IRON AND ZIRCONIUM

The iron and zirconium on the filter are dissolved in 30 c.c. of hot 1 : 3 H_2SO_4 diluted with 50 c.c. of water. Wash the paper about forty times with dilute sulphuric wash. Add to the filtrate 20 c.c. of a saturated solution of Na_2HPO_4 (di-sodium phosphate); stir well. Add 1 : 1 ammonia slowly till a precipitate just starts to form. Zirconium phosphate comes down at this stage with very little iron as the solution is still acid and most of the iron is in solution. The more zirconium with the sample the less ammonia it is necessary to add before a precipitate starts to form. After a few hours, preferably overnight, filter off the zirconium phosphate plus some iron phosphate, plus some silicon. Wash the phosphate with water forty times.

Burn it off in a weighed platinum crucible. Add about 10 drops of conc. sulphuric acid and 10 c.c. HFl. Evaporate just to SO_3 fumes. Transfer the insoluble residue into a beaker. The iron phosphate will be in solution as iron sulphate while the zirconium phosphate is insoluble. Warm the solution for a while to *redissolve the iron sulphate that may be separated out.* Filter off the insoluble residue; wash it about fifty times with water and burn it off in the same platinum crucible. (Some of the zirconium may stick to the crucible and cannot be transferred to the filter.) Burn it to a constant weight and weigh as zirconium phosphate, using the original weight of the crucible gotten just before the zirconium phosphate plus a little iron phosphate was burned in it. Multiply by 0.3836 to calculate to zirconium.

Standards were prepared by adding a known weight of metallic test aluminum and ZrO_2 (Zirconium Alba) to a plain steel; treated the same way as the samples. The recoveries are accurate. See table below.

Test Mixtures of Fe, Al, and Zr.—(1) Fuse ZrO_2 with potassium bisulphate, dissolve the melt in dilute sulphuric acid to get it in solution.

(2) Dissolve metallic aluminum in 1 : 1 HCl; fume it with sulphuric acid. Dissolve in water to get it in solution.

(3) Pour (1) and (2) into the sulphuric acid solution of the drillings of the plain steel.

RECOVERIES

Added	Found
015 gram aluminum	0164 gram aluminum
030 gram aluminum	031 gram aluminum
050 gram aluminum	0495 gram aluminum
025 gram aluminum	0265 gram aluminum
.011 gram zirconium	0108 gram zirconium
.022 gram zirconium	0214 gram zirconium
0368 gram zirconium	0365 gram zirconium
.0184 gram zirconium	0185 gram zirconium

SAMPLE OF SO-CALLED "ZIRCONIUM STEEL" SUBMITTED FOR ANALYSIS

Sample A. . .. Al, 41 per cent; Zr, 13 per cent; Si, 77 per cent.
Sample B.............. Al, 56 per cent; Zr, 17 per cent; Si, .75 per cent.

CHAPTER VII

PART II

THE COMPLETE ANALYSIS OF ZIRCONIUM-NICKEL-ALUMINUM-IRON ALLOY, FERRO-ZIRCONIUM, AND ZIRCONIUM STEEL

THIS alloy was offered as "Zirconium-Nickel," but the analysis showed it to be more of a nickel-aluminum combination.

Method.—0.5 gram of the alloy is dissolved in 90 c.c. of 1 : 1 HCl over a low flame. It is a decided advantage to get rid of the bulk of the nickel by an ammonia separation; the Al, Ti, Fe, and Zr are precipitated with 1 : 1 ammonia, adding the reagent until it is in excess and then an excess of 15 c.c. The volume at this point is about 200 c.c.

Dissolve the precipitate off the filter with hot 1 : 1 HCl; wash the filter thoroughly with HCl water about sixty times; then about ten times with water. Burn off this paper in a platinum crucible and evaporate the ash with HFl and a few drops of H_2SO_4 to remove the silica. Hold this residue to add to the main precipitate. The above HCl solution of the Al, Zr, Fe, Ti is again precipitated with an excess of ammonia to remove the rest of the nickel. This precipitate is burned off in the same platinum crucible as the first ash.

Fuse the total ash with 15 grams of $KHSO_4$, cautiously, very gradually raising the heat to low red and until all is dissolved to a clear melt. Dissolve this fusion out in 200 c.c. of H_2O plus 20 c.c. H_2SO_4 conc. Add 30 c.c. of ammonia conc.; stir well; add 1 or more c.c. of hydrogen peroxide solution to bring out the *full* brown color of titanium if any be present; and then 15 c.c. of a saturated solution of Na_2HPO_4. Let the precipitated phosphate of zirconium stand overnight in this *acid* solution; filter out the phosphate; wash the same with water thirty times; burn off the precipitate in a platinum crucible and fuse it again as before with 15 grams of the $KHSO_4$; dissolve the fusion as before with a mixture of 10 c.c. of conc. H_2SO_4 and 200 c.c. of water and add 1 c.c. or more of H_2O_2 to note if any titanium still remained with the precipitate before it was fused the second time with $KHSO_4$. Add 15 c.c. of conc. ammonia and 15 c.c. of a saturated Na_2HPO_4 solution; let stand overnight again; wash with water sixty times. Burn off the precipitate and weigh the zirconium phosphate, which contains 38.36 per cent of metallic zirconium.

If a large amount of iron be present, this zirconium will contain some phosphate of iron which must be determined by fusing the phosphate of Zr again as before with $KHSO_4$, dissolving it in 15 c.c. of conc. H_2SO_4; and 200 c.c. of water. This solution is put through the Jones reductor and the iron titrated with standard permanganate. The iron so found is calculated to ferric phosphate and deducted from the total phosphates and the remainder is calculated to zirconium by use of the factor 0.3836.

The Silicon

The silicon is found by dissolving 0.5 gram of the alloy in 90 c.c. of 1 : 1 HCl and 60 c.c. of conc. H_2SO_4 in a porcelain dish; evaporate to heavy fumes; cool and dissolve in 60 c.c. of HCl conc.; filter, wash first with dilute HCl and then with water; ignite in a platinum crucible; weigh; evaporate with HF and a few drops of H_2SO_4; ignite and weigh again; the last weight deducted from the first weight giving the silicon by difference.

The Iron, Aluminum and Titanium

The combined filtrates and washings from the two phosphate precipitations are precipitated with a slight excess of ammonia; boiled a few minutes and the combined precipitates are washed with water; burned off in a platinum crucible at the lowest red heat. The igniting of this precipitate at a high red heat renders the aluminum less soluble in the subsequent fusion with sodium carbonate. This ash is then fused with 15 grams of Na_2CO_3 at a bright red heat. The fusion is dissolved out with water in a platinum dish; filtered; the filter is washed with water. The iron and titanium will be on the filter and the most of the aluminum will be in the filtrate and washings. To extract the remainder of the Al from the Ti and Fe the filter is ashed at a low heat and again fused; leached out; filtered; washed as before with water. This filtrate and washings should contain the remainder of the aluminum. If considerable Al is contained in this last filtrate and washings from the Ti and Fe, then the latter should be ashed at a low heat and again fused, etc.

The three sets of filtrates and washings from the sodium carbonate fusions are then titrated with 1 : 1 HCl until they are just neutral to turmeric paper to precipitate the Al. Each one can be titrated separately to note the amount of Al in each. If No. 2 shows very little Al and No. 3 none or only a trace, then the operator can be certain that all of the Al has been separated from the Ti and Fe.

The Al precipitates are redissolved off the filters with hot 1 : 1 HCl; the filters thoroughly washed with water and the solution and washings are reprecipitated again with the smallest possible excess of ammonia. The reprecipitations should now be free of soda salts and can be filtered, washed with ammonium nitrate wash until free of chlorine test; the reprecipitated aluminum is then washed; ignited; and weighed as Al_2O_3 plus some phosphoric acid. After the precipitate has been blasted to a constant weight it should be fused with Na_2CO_3, at a bright red heat; the fusion is then dissolved in HCl evaporated low; converted to nitrates by two evaporations with 60 c.c. portions of conc. HNO_3, each time to 10 c.c. or as low as possible, avoiding the crystallizing of sodium salts. This solution is then boiled with a permanent excess of permanganate; cleared with iron salt and finished for phosphorus as in steel.

Calculate the phosphorus so found to P_2O_5 and deduct the amount from the Al_2O_3 plus P_2O_5 to obtain the Al_2O_3, which calculate to metal by use of the factor 0.53033. It is also advisable in close work to evaporate the Al_2O_3, P_2O_5 with a little HF and 4 or 5 drops of conc. H_2SO_4 and weigh again before, determining the P_2O_5, as a little silica is almost sure to be gathered up from the reagents and glassware in the course of the analysis. It should be always borne in mind that any filter papers from which aluminum hydroxide has been dissolved should, after thorough washing with nitrate wash (5 grams of ammonium nitrate in 500 c.c. of distilled water), be ashed and saved as part of the aluminum, as aluminum hydroxide is difficult to dissolve and entirely wash out of a filter paper.

TITANIUM AND IRON

The residue on the filter from the second or third fusion with sodium carbonate to remove the aluminum from the iron, titanium; aluminum ash, will contain all of the iron and titanium now free of Al. Dissolve this residue off the filter with 30 c.c. of conc. HCl diluted with 30 c.c. of water. Pour this acid back and forth, hot, over the filter until all the residue is completely dissolved. Wash the filter thoroughly with dilute acid wash and then with water. Dilute the filtrate and washings to 200 c.c. Divide into two portions, taking one portion for the iron and the other for titanium.

To each portion add 30 c.c. of conc. H_2SO_4 and evaporate them to thick fumes. Add 150 c.c. of water to the iron portion and boil until all salts of iron are in solution. With volume still at 150 c.c., pass the solution through the zinc reductor slowly and titrate it with standard $KMnO_4$ for iron in the usual way.

The *titanium* half is made almost ammoniacal and 10 grams of hyposulphite of sodium are added and heated; the titanium is precipitated; it is filtered off; washed fifty times with sulphurous acid water (5 c.c. of conc. H_2SO_3 in 500 c.c. of water). The titanium precipitate is burned off, and if it is not white it is fused with 10 grams of $KHSO_4$. The melt is dissolved out with 30 c.c. of conc. H_2SO_4 diluted with 150 c.c. of water; made neutral with ammonia and again precipitated as before by boiling with 10 grams of "hypo." This precipitate is washed; ignited and weighed as TiO_2, which is calculated to Ti by use of the factor 0.60049.

RESULTS OF ANALYSIS OF SO-CALLED "NICKEL-ZIRCONIUM" ALLOY

Carbon	0 06
Manganese	0 06
Nickel	70 30
Zirconium	7 85
Aluminum	12 98
Iron	3 67
Silicon	4 87

It will be seen by the above analysis that the true properties of zirconium nickel are far from being demonstrated by such a conglomeration of high and low melting-point elements. It is 100 per cent more of a nickel-aluminum-silicon alloy than it is a nickel-zirconium one

Test Method, Formulas and Calculations.—The following is a convenient mixture to test one's skill in carrying out the foregoing method: 3 grams of nickel ammonium sulphate, 150 grams of zirconia "alba," which is sold as 99.5 per cent ZrO_2, and 0.046 gram of aluminum wire assumed to be 99.5 per cent pure. This mixture should contain 0.110 gram of Zr, as ZrO_2 contains 73.89 per cent Zr. From such a mixture 0.110 gram of Zr was recovered; and when 0.0995 ZrO_2 were added 0.0984 gram of ZrO_2 was found. In the latter case the zirconium was precipitated from a volume of 300 c.c. in the presence of 7 c.c. of free conc. H_2SO_4 with 15 c.c. of a saturated solution of sodium-hydrogen phosphate. The zirconium, when precipitated in the presence of considerable iron, will carry out considerable iron as phosphate, even after reprecipitation. After the final weighing as phosphate the iron is determined and deducted as already described. Assuming that the iron is present as phosphate, $FePO_4$, which contains 37.00 per cent of metallic iron, then the iron found by passing the dissolved zirconium phosphate through the reductor is divided by 0.37 and the amount of phosphate of iron so found is deducted from the weight of the impure zirconium phosphate giving the weight of the iron-free phosphate of zirconium.

The metaphosphate of zirconium so obtained is given as $5ZrO_2, 4P_2O_5$, when ignited; and unignited is given as including $8H_2O$. The ignited salt would therefore contain 51.88 per cent ZrO_2 or 38.36 per cent Zr. Dr. W. F. Hillibrand gives as reference, Gmelin-Krauts Handbuch d. anorganischen Chemie, II, 1, p. 703.

THE ANALYSIS OF FERRO-ZIRCONIUM AND ZIRCONIUM STEEL FOR ZIRCONIUM

The following method is given so as to apply even when much chromium and tungsten are present:

Digest 1 gram of steel or 0.5 gram of ferro-zirconium with 50 c.c. of 1 : 3 sulphuric acid until action ceases; add 50 c.c. of 1.20 HNO_3 and take to fumes of SO_3; cool; add 60 c.c. of 1.20 nitric acid and take to fumes again; cool; add 100 c.c.

See also page 191.

of 1 : 1 HCl and boil for ten minutes; add a paper pulp and filter into a 600 c.c. beaker. Wash well with 1:30 HCl until the washings give no iron test; then wash twenty times with water. Hold the filtrate and wash the tungsten residue on the filter paper with ammonia water. During this washing with ammonia water, stir up the pulp on the filter well, turning the same completely over. After the yellow color is all gone from the filter, it should be washed many times more to insure the perfect removal of the tungsten salt. This will require at least sixty washings with frequent turning over of the pulp mass on the filter. As the washed filter and pulp may contain some of the Zr, it is burned with the main Zr phosphate precipitate obtained from the main iron and chromium filtrate from the tungstic acid in the following manner:

This filtrate and washings containing the main Fe, Zr, and Cr are taken to fumes after adding 50 c.c. of 1 : 3 H_2SO_4. The residue in the dish is dissolved in 100 c.c. of water with heat and then made *faintly* but distinctly ammoniacal; add exactly 4 c.c. of conc. H_2SO_4; stir until all of the precipitate obtained with ammonia is dissolved, then add 15 c.c. of a saturated solution of Na_2HPO_4 and then 300 c.c. of water and let stand overnight.

The precipitate of zirconium phosphate so obtained should be washed well with water; burned off with the filter and pulp remaining after the removal of the tungstic acid with ammonia wash. The ash should contain the total zirconium together with a little chromium; ash from paper; and some iron that is always retained as phosphate. Weigh the total ash after blasting five or six minutes. Add to this weighed ash 3 drops of 1 : 3 H_2SO_4 for steel (in case of a ferro-zirconium, add enough sulphuric acid to thoroughly moisten the ash) and 15 c.c. of HFl. Heat and evaporate to dryness; ignite and weigh. The weight at this point equals Zr and a little Fe. Then fuse the weighed Zr plus Fe residue with 15 grams $KHSO_4$; dissolve in 200 c.c. of water and 20 c.c. conc. H_2SO_4; take to fumes of SO_3; cool; add 100 c.c. of water; boil; and cool again. Run the solution slowly through the zinc reductor which will reduce the iron but not the zirconium. Titrate the iron with standard permanganate; calculate the metallic iron so found to ferric phosphate by dividing its weight by the factor 0.37; deduct the amount of ferric phosphate so found from the total weights of the phosphates of Fe and Zr.

Calculate the remainder to Zr by multiplying by the factor 0.3836 ($5ZrO_2, 4P_2O_5$).

Test Mixtures.—To test one's manipulations, 0.020 gram of ZrO_2 can be fused with 5 grams of $KHSO_4$; dissolved as already described and the solution is added to the H_2SO_4 solution of the steel or if a ferro-zirconium is being analyzed a correspondingly larger amount of the zirconia alba can be used and added to the sulphuric solution of a plain steel. When larger amounts of zirconium, iron, and chromium are to be separated, considerable free acid is necessary to keep back the iron and chromium. For example, it was necessary in one case to add as much as 15 c.c. of free conc. H_2SO_4 in a 600 c.c. volume to hold back a big precipitate of iron from coming down with the zirconium. Even with this large amount of free acid some iron phosphate was found with the zirconium phosphate.

By the above method the following recoveries were made from a high tungsten-chromium steel:

Amount of Fused ZrO_2 Added	Amount of ZrO_2 Found
0.0149 gram	0.0135 gram
0.0143 gram	0.0143 gram
0.0144 gram	0.0142 gram
0.0297 gram	0.0290 gram

RECOVERIES FROM PLAIN STEEL—NO Cr PRESENT

Amount of Fused ZrO_2 Added	Amount of ZrO_2 Found
0.0199 gram	0.0190 gram
0.00186 gram	0.00190 gram

(See Rapid Method Using Ammonia. Page 191)

SILICON

Fuse at a low heat 0.6 gram with mixture of 3 grams of sodium carbonate and 6 grams peroxide in an iron crucible. Heat until all is melted; about five or six minutes is enough. Longer heating only causes the iron crucible to be heavily cut. Dissolve fusion out in water; clean the crucible with a little acid, acidulate water solution of fusion with excess HCl and heat until all iron is in solution. Add 45 c.c. of conc. H_2SO_4 and evaporate it to heavy fumes of SO_3. Cool, and then add some water and heat it again till all iron is dissolved; add a little sulphuric acid if necessary.

Filter off silicon; wash it free of iron with a sulphuric wash; smoke off the paper and heat until residue is white. Weigh, then evaporate the ash with HF and sulphuric acid to fumes; heat to redness and weigh again. Loss of weight less blank from reagents equals the silicon.

ZIRCONIUM

Warm in the platinum crucible in which the silicon was evaporated a few drops of 1 : 1 HCl to dissolve any trace of iron left therein and add this solution to silicon filtrate. Concentrate the latter to remove excess of free acid; peroxidize with sodium peroxide and finish as for zirconium in plain steel.

When zirconium only is asked for weigh 0.5 gram of sample in a platinum dish; add slowly 15 c.c. of HF; warm it for a while; then add conc. HNO_3 a few drops at a time till action ceases. Add 10 c.c. conc. H_2SO_4 and take it to heavy fumes of SO_3. Cool it, add water, and heat it again till iron is dissolved. Transfer to a 600 c.c. beaker and finish as in plain zirconium steel.

CHAPTER VII

PART III

THE QUANTITATIVE SEPARATION OF ZIRCONIA FROM IRON, TITANIUM, ALUMINUM, AND SILICA AND THE ANALYSIS OF CRUDE ZIRCONIA (ZIRKITE)

WEIGH 0.3 or 0.4 gram of the finely ground mineral; and fuse it with 15 grams Na_2CO_3 in which has been thoroughly mixed 0.5 gram of KNO_3. Keep the mass in a molten condition for twenty minutes; cool; dissolve out the melt in water; transfer from the platinum dish to porcelain; add 50 c.c. of conc. HCl, or enough to make the solution acid; boil off the CO_2 with the vessel covered; add 60 c.c. of 1 : 3 H_2SO_4; evaporate to thick fumes of SO_3. Cool; add 100 c.c. of water; heat until all salts are in solution; filter and wash with 1 : 40 H_2SO_4 about fifty times.

Place the residue on the filter in a platinum crucible; smoke off the paper and heat until all of the filter is gone; weigh; add 15 c.c. HF and 10 drops of conc. H_2SO_4 to remove the silica by evaporating. Remove the excess of the HF and H_2SO_4; heat to redness; cool and weigh; calculate the loss of weight as usual to silica. The residue should be again treated with some hydrofluoric and sulphuric acids; evaporated; ignited and weighed to insure the complete removal of all of the silica.

The residue left in the crucible after the complete removal of the silica is fused with 3 or 4 grams of $KHSO_4$; dissolved out in water and the solution is combined with the main filtrate from the crude silica. Add a slight excess of ammonia and then add 10 c.c. 1 : 3 H_2SO_4. Precipitate from this acid solution, which should have a volume at this point of 500 c.c. the zirconia as phosphate, using 20 c.c. of a saturated solution of di-sodium phosphate, and 20 drops of H_2O_2. Let stand overnight; wash about twenty times with water. The filtrate should contain most of the iron, aluminum, titanium, and manganese. To insure a complete separation of the zirconium, the zirconium phosphate, after ignition in a platinum crucible, is fused with 10 grams of $KHSO_4$ until a clear melt is obtained. The melt is dissolved out in water. The solution is made slightly ammoniacal; and then 10 c.c. of 1 : 3 sulphuric acid are added. The zirconium is then reprecipitated as phosphate as before; filtered; and washed thoroughly. It is now free of iron, titanium, etc. It is burned off and weighed as pure phosphate of zirconium which weight is calculated to ZrO_2 by use of the factor 0.519. The phosphate precipitation is made in a volume of 600 c.c. The zirconium phosphate should be washed at least sixty times with water to insure the removal of the excess of the precipitant. All of the Fe, Ti, Al, Mn are contained in the two sets of filtrates and washings from the two precipitations of the zirconium phosphate. To these filtrates add a slight excess of ammonia which will precipitate the iron, aluminum, and titanium. Heat to boiling for five minutes; filter wash thoroughly with water; burn off in a platinum crucible at a *low red heat*. Do not ignite, as it will render the aluminum more difficult to fuse. Fuse the residue in the crucible with twenty times its weight of sodium carbonate. Dissolve the melt in water; filter out the water-insoluble residue; wash it with water containing 5 grams of sodium carbonate per 500 c.c. Roast out the paper from this residue; fuse it; dissolve it out in water as before; filter it; wash; and render the two sets of filtrates neutral to turmeric paper as described on page 195. The aluminum is then finished as described on page 196. Burn off the iron and titanium residue remaining after the removal of the aluminum by two fusions with sodium carbonate and the leaching out with water. Fuse the ash with sodium carbonate; dissolve out in water; acidulate with HCl; heat until all CO_2 is gone; transfer the clear solution to a 250 c.c. volumetric flask; dilute to the mark; evaporate one portion (125 c.c.) to thick fumes with 20 c.c. of 1 : 3 H_2SO_4; add 100 c.c. of water and heat until all but floating matter, if any, is dissolved; dilute to 400 c.c.; add a slight excess of ammonia; then add 2 or 3 c.c. of 1 : 3 H_2SO_4 (slight excess). Then add 10 grams of $N_2S_2O_3$; boil thirty minutes and finish for titanium as described on page 51 for titanium. Multiply the weight of TiO_2

so obtained by two to obtain the amount of it present in the original weight of sample taken for the analysis.

The other 125 c.c. of the solution of iron and titanium is reduced by stannous chloride as described on page 443 for Iron.

RESULTS OBTAINED ON KNOWN MIXTURES

Added Grams of ZrO_2	Found Grams of ZrO_2
Added gram of 0 297 ZrO_2	Found gram of 0 294 ZrO_2
Added gram of 0 014 Fe_2O_3	Found gram of 0 0128 Fe_2O_3
Added gram of 0 0186 Al_2O_3	Found gram of 0 0183 Al_2O_3
Added gram of 0 0099 TiO_2	Found gram of 0 0094 TiO_2

RESULTS OBTAINED FROM A SAMPLE OF CRUDE ZIRCONIA

72 25 ZrO_2; 4 40 Fe_2O_3; 2 35 Al_2O_3; 2 05 TiO_2;
16.00 SiO_2; 0 64 MnO_2; 1 73 ignition; 0 87 CO_2.

CHAPTER VIII

PART I

COPPER IN STEEL AND PIG IRON

DISSOLVE 15 grams of drillings in 300 c.c. of 1.20 nitric acid in an 800 c.c. beaker. Heat until all action ceases. Add an excess of $KMnO_4$ solution of the same strength as used for phosphorus in steels. Boil gently for thirty minutes. If the $KMnO_4$ disappears during the boiling, add more of it. Steels require from 4 to 8 c.c. and pig iron from 25 to 30 c.c. of the permanganate solution.

In pig iron add 5 c.c. of hydrofluoric acid before boiling with permanganate of potash. Heat ten minutes. Then boil with the $KMnO_4$ solution.

After boiling the pig iron or steel with permanganate solution, add enough wet pulp to nearly fill a 50 c.c. graduated cylinder. Filter through double 12 cm. filters into an 800 c.c. beaker. Wash the pulp, etc., partly free from iron with a dilute nitric acid wash consisting of 5 c.c. of 1.20 nitric acid diluted with 200 c.c. of water. This takes about forty washings.*

To pig iron or steel containing from 0.010 to 0.030 per cent of copper, add at this stage 20 c.c. of a solution of potassium ferricyanide, made by dissolving 5 grams of the crystals in 120 c.c. of distilled water. Stir thoroughly and permit the solutions to stand.

If the copper content is unusually high, add 2 c.c. of the ferricyanide solution for every milligram of copper supposed to be present in the steel. If nickel is present, it is precipitated with the copper, but forms more slowly.

As there is a tendency to form blue cyanide of iron the filtrations should be proceeded with in about a half hour. Add as much paper pulp as in the first filtrations, filter and wash five or ten times with water containing 5 c.c. of ferricyanide solution per 100 c.c. of distilled water. Use a 15 cm. filter.

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* Read near the top of page 208 concerning the addition of ammonia to prevent excessive formation of iron cyanide.

Roast off the pulp in a porcelain crucible. Dissolve the iron, nickel and copper oxides with 5 c.c. of conc. hydrochloric acid. Rinse the solution into a 200 c.c. beaker. Dilute to 150 c.c. with water and pass H_2S for a half hour at a rapid rate. This removes the copper from nickel and any iron that may have been precipitated as cyanide.

Filter on a small filter; wash twenty times with H_2S water. Burn the paper in a 45 c.c. porcelain crucible. Dissolve the oxide in 20 c.c. 1.20 nitric acid, warming until all black residue is dissolved except perhaps an occasional flake of carbon from the filter paper. Rinse the solution into a 5 ounce beaker, keeping the volume as low as possible for copper of 0.020 per cent and under, in order that the blue color with ammonia may be distinct. Copper as low as 0.015 per cent gives a distinct blue if properly manipulated. Now add a saturated solution of sodium carbonate, a little at a time, until a precipitate forms. Then add 0.5 c.c. of conc. ammonia. Titration follows with a standard solution of potassium cyanide, made by dissolving 2.244 grams of potassium cyanide and 5 grams of stick potassium hydroxide in water and diluting to 1000 c.c. One c.c. of this standard should equal about 0.00064 to 0.00069 gram of metallic copper. Standardize the solution by adding 10 and 15 mgs. of metallic copper of 99.8 per cent Cu to 15 grams of any steel or pig iron. Weigh out also two 15 gram portions of this same steel or iron, but add no copper to them. Put all four weights through the entire operation, titrating each one to the disappearance of the blue as given under "Titration."

Titration.—Place a 5 ounce beaker containing distilled water beside the one containing the copper to be tested. Add the cyanide standard to the test until it is as free from even a slight blue tint as the beaker of distilled water.

This method has been tested with known amounts of copper added to steels, and with steels standardized by the old standard methods. It is much more rapid, and results check very satisfactorily. Filtrations might be hastened by using pulp filters on porcelain plates and applying slight suction.

CALCULATIONS

Pig Iron Sample.

(1) 16.0 second reading of burette.
7.9 first reading of burette.

8.1 equals c.c. of standard used.
No copper added.

(2) 48.0
15 mgs. copper added 16.2

31.8 equals c.c. of standard used.

(3) 10 mgs. copper added 23.6
0.0

23.6 equals c.c. of standard used.

(4) 31.8−8.1 equals c.c. of standard used by 15 mgs. Cu.

(5) 23.6−8.1 equals c.c. of standard used by 10 mgs. Cu.

(6) From (4) we have 15÷23.7=0.632, or 1 c.c. of cyanide equals 0.000632 gram Cu. (0.998×15÷23.7.)

(7) From (5) we have 10÷15.5=0.643, or 1 c.c. of cyanide equals 0.000643 grams Cu. (0.998×10÷15.5.)

(8) From (1) we have 8.1×0.00064÷15×100=0.0345, or 0.0345 per cent copper in the sample of pig iron, 15 grams having been taken for analysis.

Qualitative Value.—With 2 grams of sample as little as 0.1 per cent of copper gives a very noticeable yellowish cloud when the potassium ferricyanide is added to a solution of steel treated as described. Hence the method affords a rapid qualitative test for the presence of copper in sufficient quantity to be injurious (0.05 per cent and over) for *most* purposes for which fine tool steel is used. The operator can easily decide whether the precipitate is copper or nickel. If it is copper, the precipitation is almost instantaneous. If it is nickel, the reaction is noticeably slower and the precipitate is of a brown color, closely resembling that of iron hydroxide. A yellowish cloud, forming, at once, on the addition of the first c.c. of the precipitant, is characteristic of copper. If this be followed by a more slowly forming brown precipitate,* then both elements are present. Many makers of tool steel insist that the copper content of best tool steel be under 0.02 per cent. Several steels doing fine work, however, have been analyzed by the author and found to contain copper greatly in excess of this limit. It is largely a question of what sort of a tool is to be made from the steel.

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* Add at least 20 c.c. of the ferricyanide when testing for nickel.

The tendency to form blue ferricyanides of iron on adding potassium ferricyanide to ferric solutions, the author has found can be eliminated sufficiently to prevent serious clogging of filters, by keeping the iron solution somewhat neutral, after *first boiling it with an excess* of permanganate solution and filtering out the excess of manganese oxide. After removing the latter by filtration, add 1 : 1 ammonia until the hydroxide of iron dissolves rather slowly.* Then add the ferricyanide and proceed as already described. *Keep the solution still quite acid.*

As the copper ferricyanide precipitates almost instantly, forming a very considerable cloud of yellowish precipitate even with 0.03 per cent copper, it is very finely divided, and has a tendency to run through the filter. The first portion that is filtered should be poured back on the paper until it runs through clear. Then proceed with the filtration. Stand the main filtrate aside when washing begins, and, should the latter be cloudy, filter with a little pulp on a small filter and add it to the main precipitate.†

When precipitating a large quantity ‡ of copper by this method—for example, 60 or 100 milligrams—the somewhat acid solution should be largely diluted, making the volume from about 800 c.c. before adding the precipitant. (See Separation of Copper and Nickel from Vanadium by Ferricyanide of Potassium.) It is better to precipitate such large amounts of copper with H_2S.

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* Do not carry the neutralization too far as in nearly neutral solutions the nickel and copper precipitate very slowly with the ferricyanide.

† Pay no attention to any clouding of the filtrate that may occur after the latter has stood for some time.

‡ The foregoing method is especially useful for very small per cents of Cu and Ni, i.e., 0.100 down to 0.005 per cent, as from 15 to 20 grams of sample can be taken For higher per cents it is easier to weigh out from 1 to 3 grams of plain carbon steel; dissolve in 1 : 1 HCl and pass H_2S at once. Then finish as in the ferricyanide method from the point where H_2S was passed through the solution of the copper and iron oxides. Examine all insoluble residues for Cu.

The ferricyanide method is the best for high-speed steels. See page 212, the bottom paragraph.

For accurate work all insoluble residue from steel dissolved in sulphuric or hydrochloric acids should be examined for copper by filtering the same out; washing it; igniting it; fusing with twenty times its weight of sodium carbonate and twice its weight of niter in a platinum crucible. The fusion is dissolved out in water; transferred to a beaker acidulated with an excess of HCl; evaporated low and added to the main solution of the sample before saturating it with H_2S. The insoluble residues are almost certain to contain part of the copper.

Small Amounts of Copper and Nickel in Steel and Iron.—When analyzing steel, iron, etc., for copper, do not carry the neutralization, given on page 208, too far, as in nearly neutral solutions, small amounts of nickel ferricyanide precipitate very slowly, and the precipitation of the copper ferricyanide is also delayed.

The method described for copper on pages 200 to 207 is designed for small amounts of copper, that is, for percentages ranging from 0.100 to 0.001 and for equally low per cents of nickel. If nickel in such small per cents is asked for, get the ferricyanide precipitates of the nickel and copper together in the same way as directed on pages 200 to 207 using 15 grams of sample and the same method of solution as given for copper in steel, separating the nickel from the copper and determining it as given on pages 210 to 212.

Large Amounts of Copper in Plain and Alloy Steels.—If the percentage of copper exceeds 0.100 per cent, then dissolve but 1 or 2 grams of the sample, and proceed as described. If the sample is an alloy steel, then it is necessary to decompose the same in the manner given for chromium tungsten steel on pages 5 to 7, whether the amount of copper be large or small. If the amount is small then 15 grams should be taken for the analysis and a proportionate amount of sulphuric acid followed by an equal amount of the 1.20 nitric acid, that is, 200 c.c. of the 1 : 3 sulphuric acid; and after the action of this acid is over, aided by heating for a half hour, then 200 c.c. of the 1.20 nitric acid are added and the analysis is finished as for copper in plain carbon steel.

CHAPTER VIII

PART II

SEPARATION OF NICKEL AND COPPER FROM IRON AND VANADIUM BY POTASSIUM FERRICYANIDE

PROCEED as outlined for copper in steel, except smaller weights of sample are usually required.

For nickel and copper in ferro-vanadium dissolve 1 or 2 grams of sample, using 30 c.c. of 1.20 nitric acid for each gram. If the ferro is high in silicon, carbon and aluminum, and for this reason only partly soluble in nitric acid, add a few c.c. of hydrofluoric acid to the solution after action with nitric acid is over. Heat until all metallic or gritty particles are in solution. Or the insoluble part can be broken up by a sodium carbonate and niter fusion; dissolved in hydrochloric acid; the latter removed by evaporation to fumes with sulphuric acid; the sulphate dissolved in water and returned to the main solution. Then boil the latter with an excess of permanganate solution; filter out the manganese oxide as described under Copper in Steel. To the filtrate and washings 1 : 1 ammonia is added until a slight precipitate of hydroxide is obtained that dissolves slowly. The copper and nickel are precipitated with potassium ferricyanide as in Copper in Steel. Large amounts of nickel—i.e., from 0.025 to 0.050 gram—precipitate quickly, but smaller quantities should be permitted to settle for one hour before filtering. It is best to let all nickel tests stand at least one hour. Add as much paper pulp from ashless filters as will nearly fill a 15 cm. filter. The precipitate and pulp are filtered out; washed a few times; dried; ignited in a large porcelain crucible; the ash transferred to a 6 ounce beaker; dissolved in 30 c.c. of aqua regia. Clean the crucibles with 10 c.c. of the latter and add the cleanings to the main part. (Nickel oxide dissolves with some difficulty, requiring considerable heating.) 50 c.c. 1 : 3

sulphuric acid are added to the solution; evaporated to 12 c.c.; diluted to 300 c.c.; the copper is precipitated with H_2S; filtered out and washed thoroughly with H_2S water and finished as in steels. The filtrates and washings from the H_2S precipitation will contain all of the nickel and a little iron. Evaporate this filtrate and washings to 50 c.c., and add 30 c.c. of conc. nitric acid to oxidize the iron and destroy any remnant of the H_2S. Heat with a cover on the dish until all action is over. Then remove the cover, cool, add 30 c.c. 1 : 3 sulphuric acid and evaporate until slight fumes of sulphuric anhydride are obtained. Cool; add 50 c.c. of water; and filter into a 600 c.c. beaker. Add 10 grams of citric acid; make faintly ammoniacal; cool and titrate the nickel with potassium cyanide. (See the author's modified cyanide method for Nickel in Steel, page 220.)

If it is desired to determine a very small quantity of nickel in steel, about 0.3 per cent and under, weigh 10 or 15 grams of sample and proceed as outlined, getting the nickel and the copper from the one analysis. If the nickel content is likely to be under 0.1 per cent, it is convenient to use 10 grams of sample. If it is in excess of 0.2 per cent, it is best to use 5 grams. The precipitate requires that considerable paper pulp be mixed with it to secure rapid filtrations. Wash the pulp, etc., five times with water containing a drop of sulphuric acid and 5 c.c. of the ferricyanide solution per 100 c.c. of water. As the precipitate has a tendency, at times, to run through the filter when first poured on it, this first portion of the filtrate is refiltered until it is clear. When filtering large precipitates, such as would be obtained from 50 mgs. of nickel, it is expedient to use two funnels to hasten matters. Nickel up to 50 mgs. from a 5 gram weight of sample, or 10 mgs. of nickel from 10 grams of sample, can be conveniently precipitated from a volume of 500 c.c. For large amounts of nickel in steel,—i.e., 0.50 per cent and over,—the foregoing method is not nearly so rapid as the one described on pages 220 to 234, but for minute quantities, or where it is necessary to remove the bulk of the iron or the vanadium (much vanadium in solution gives ammoniacal citrates of an almost greenish black color,* greatly interfering in the method just referred to), it is a useful preliminary to the cyanide titration. There would seem to be no reason why the ferricyanide could not be applied, with suitable modifications, to the determination of copper and nickel in ferro-manganese, chrome and other ferros and metals that are not precipitated by this useful reagent (notably aluminum) in acid solution. Manganese is precipitated by the ferricyanide in neutral or slightly ammoniacal solution as quickly as are copper, nickel, and zinc in slightly acid solution. (See the author's method for all percentages of manganese, page 69.)

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* Read page 32.

By the above process the copper and nickel can be determined, quantitatively, in the same analysis with the chromium and the vanadium when the copper does not greatly exceed 0.25 per cent: Two grams are taken for the analysis. The nickel and copper ferricyanides are filtered out after the regular titrations have been made for V and Cr. Of course no time must be lost in making the vanadium part of the titration, as copper soon clouds the solution after the addition of the ferricyanide. The author uses this scheme to get Cr, V, Ni and Cu from the one analysis. In such cases the titrated solution is allowed to stand a half hour before filtering. If brown nickel ferricyanide begins to appear, 40 or more c.c. of potassium ferricyanide are added and filtration is delayed for an hour.

CHAPTER VIII

PART III

COPPER IN METALLIC COPPER VOLUMETRIC

THE author regards the following cyanide titration as a simple and rapid method for the assay of metallic copper. Scarcely any element interferes that cannot be removed by precipitation with H_2S in hydrochloric acid solution. If carried out with proper attention to details, there is no more accurate volumetric method in commercial use. It is essential that the potassium cyanide be standardized with metallic copper of known copper content, or by some recrystallized c.p. salt of copper. The metal is preferable, and is put through every analytical detail that is applied to the analysis of the test.

Operate with 0.5 gram of the test and of the standard copper drillings, running both standardizations and tests parallel with each other. Use copper of 99.8 per cent purity for standardizing. The drillings are dissolved in 10 c.c. 1.20 nitric acid, evaporated to 5 c.c., filtered from any tin, etc.; the filter washed with water containing a little nitric acid. The filtrate and washings are evaporated to fumes with 20 c.c. 1 : 3 sulphuric acid. The copper sulphate is dissolved in water. Any lead is removed by filtration and washed with water containing a little sulphuric acid. Hydrogen sulphide is then passed through the filtrate, in a volume of 400 c.c., with 5 c.c. excess of 1 : 1 hydrochloric acid for every 100 c.c. of water, until the copper has completely separated in hot solution. Filter. Wash with H_2S water. Return filter and all to the beaker. Add 50 c.c. of 1.20 nitric acid. Give standardizations and test the same excess of acid. Warm with a cover on until copper sulphide is dissolved. Filter out pulp. Wash thoroughly with water containing a little 1.20 nitric acid. Ignite the pulp; dissolve the residue in 1.20 nitric acid; add the solution to the filtrate and washings; evaporate to 20 c.c. Add 1.5 grams of citric acid and a slight excess of sodium carbonate. Use a saturated, filtered solution of the carbonate and add it until effervescence ceases entirely. Titrate the clear blue solution with a standard of potassium cyanide made by dissolving 22.434 grams of the best cyanide together with 5 grams of potassium hydroxide in distilled water and diluting to 1 liter. One c.c. of this standard usually equals about 0.00635 gram of copper; but this value should always be fixed by the operator himself, in the manner just outlined. The following modification removes uncertainty as to the end-point when titrating large amounts of copper. Add the potassium cyanide as usual until the blue color is almost gone. Follow with additions of a cyanide standard of one-fifth strength until all blue tint has disappeared.* Then add 2 c.c. of a 20 per cent solution of potassium iodide in water; then silver nitrate standard until a slight cloud of silver iodide is formed as in Nickel in Steel. (Chapter IX.) Now add about 10 c.c. excess of this dilute cyanide standard. Again add the silver nitrate standard until a slight milkiness is produced in the solution; 2.925 grams of silver nitrate are dissolved in water and diluted to 500 c.c. for this work.

Standardization.—Suppose 0.500 gram of copper drillings of 99.8 per cent purity were taken, and that after putting this metal through all of the foregoing analytical operations the following data were obtained:

First, the concentrated cyanide standard required to *nearly* discharge the blue color equals 76.9 c.c.

Second, the one-fifth cyanide standard required to *entirely* discharge the blue equals 26.8.

Third, the silver nitrate solution needed to produce a slight milkiness in the solution, after the blue color was entirely gone, equals 13.6 c.c.

Fourth, 8.3 c.c. of silver nitrate were used to produce a cloudiness, again, after the addition of 11.3 c.c. of the one-fifth cyanide standard in excess, or 1 c.c. of $AgNO_3 = 11.3 \div 8.3$, or 1.36 c.c. of the one-fifth cyanide standard.

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* Now wait for thirty minutes to one hour to give the KCN and the copper time to completely react together before adding the KI and silver nitrate to get the excess of KCN. This should be done because the blue color of the copper disappears long before the copper and the KCN have entirely ceased to combine.

Fifth, therefore $26.8-(13.6\times 1.36)=8.3$, or the amount of one-fifth cyanide used in reaction with the copper, or 1.66 c.c. of conc. cyanide to be added to 76.9, or a total of 78.56 c.c. of conc. KCN required to combine with the 0.500 gram of 99.8 per cent pure copper. Hence 1 c.c. of the concentrated cyanide standard equals $0.499\div 78.56=0.00635$, or 1 c.c. $=0.00635$ gram of copper.*

Mr. R. M. Clarke of this laboratory suggested that it might be an advantage to use silver nitrate to obtain a more exact end-point instead of relying on the disappearance of the blue. The analytical details are the author's.

Further Details.—(*a*) Stir the copper sulphide into small particles before heating it with the 1.20 nitric acid, or an insoluble black lump may form. Then heat very gently at first. Keep the temperature considerably below 100° C. at all times to prevent occlusion of some of the copper sulphide by the liberated sulphur, and the formation of a black insoluble residue. Pay no attention to any milkiness that may appear when the nitric acid solution of the pulp ash is added to the nitric solution of the main sulphide.

(*b*) The titration can be accurately accomplished, omitting the one-fifth cyanide standard: Add the concentrated standard until the blue is entirely gone.† Then add the KI indicator and follow with the silver nitrate until a very slight permanent cloudiness occurs. Next drop into the beaker an excess of 5 c.c. of the conc. cyanide. Again add the silver nitrate until a very faint milkiness is once more apparent that does not disappear after 15 seconds stirring.

(*c*) Further, it is quite important to add the cyanide, while discharging the blue color, very slowly when the latter begins to fade: Add the standard 3 drops at a time; then stir vigorously for twenty seconds. If the blue is not all gone, add 3 drops more and stir again for a period of twenty seconds. By proceeding in this way and making the titrations in small volumes —beginning with a volume of not over 100 c.c.—the disappearance of the blue affords an accurate end-point but more experience and judgment is required than when using the cyanide and "silver" scheme. After thus carefully removing the blue tint proceed to determine the actual cyanide used by means of titration (*b*).

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* The author now uses one-half this strength, or 1 c.c. equals 0.003175 gram of copper. A 100 c.c. burette, graduated to $\frac{1}{10}$ c.c., is the best adapted to this method.

† Then pause for at least thirty minutes before adding the KI.

Calculations.—(1) 0.500 gram of copper required 84.2 c.c. of the concentrated cyanide to just discharge the blue.

(2) 24.8 c.c. of the $AgNO_3$ standard were required to produce the *first* faint cloudiness.

(3) 21.9 c.c. of $AgNO_3$ were needed to produce the second faint cloud after the addition of 5 c.c. excess of the conc. KCN. Therefore $21.9 \div 5 = 4.38$, or 1 c.c. of the cyanide equals 4.38 c.c. of the silver nitrate standard.

(4) From (2) and (3) we have $24.8 \div 4.38 = 5.66$, or the excess of the cyanide standard in the solution. From (1) $84.2 - 5.66 = 78.54$, or the number of c.c. of the cyanide required to combine with the 0.500 gram of copper. There is always an excess of the cyanide when the blue color is gone, but the reaction between the copper and the KCN is not usually completed for at least thirty minutes after the disappearance of the blue.

TITRATION OF COPPER IN THE PRESENCE OF OTHER METALS

If the solution contains 3 grams of citric acid and a moderate excess of the sodium carbonate, 0.500 gram of copper can be accurately titrated in the presence of 0.100 gram of zinc, or iron, or 0.050 gram of lead: The citric acid is added to the nitric solution of the metals; then the carbonate until effervescence ceases, and 5 c.c. in excess. The volume before titration should be about 100 c.c. When much iron is present the alkaline solution is a dark green. The cyanide standard is added until the green is gone and the clear amber color of the citrate of iron appears. Then determine the excess of the cyanide as usual.

As much as 0.100 grams of arsenic can be present without having the slightest effect.

The author made entirely successful titrations of 0.500 gram of copper dissolving with it 0.200 gram of antimony; also in the presence of 0.100 gram of cadmium. This end-point given by the disappearance of bluish tints from the white antimony oxides and cadmium carbonate was noted. The end-point was obtained as in (*c*). The precipitates were then removed by filtration through double filters, and the excess of cyanide was determined in the filtrate and washings in the usual way with silver nitrate. The precipitates had to be poured through the filters several times to secure clear filtrates. The precipitates were washed ten times with dilute sodium carbonate water.

When titrating copper in the presence of 0.200 gram of bismuth the disappearance of the blue was taken as the end-point, as the basic bismuth clouded the solution. With but 0.100 gram of bismuth in solution the entire titration, as outlined in (*b*), was successfully carried through before the solution was perceptibly clouded.

Large quantities of manganese interfere with the titration of copper only in so far as dark-colored solutions are formed when the cyanide is added, thereby obscuring somewhat the end-point between the cyanide and the "silver nitrate." More citric acid is required. Add to the standardization about as much manganese as there is likely to be in the copper that is to be assayed. Use at least 6 grams of citric acid per 0.200 gram of Mn.

PRECIPITATION BY ALUMINUM

When using this well-known method one can proceed as at first described until the filtrate and washings from the lead sulphate are obtained. Evaporate the former to 20 c.c.; add 10 c.c. 1 : 3 sulphuric acid and a piece of aluminum $1\frac{1}{2}$ inches square by $\frac{1}{16}$ inch thick. Heat nearly to boiling for thirty minutes, or until the solution is colorless. Remove the aluminum and decant the solution through a 9 cm. filter; wash the filter fifteen times with water containing a few drops of 1 : 3 H_2SO_4. Return the filter to the 150 c.c. beaker in which the precipitation was made.

The filtrate and washings from the metallic copper should be tested with H_2S and, if a brown coloration is obtained, continue to pass the gas until the small precipitate of copper collects. Filter it out; wash it with H_2S water containing a drop or two of 1 : 3 H_2SO_4. Put this filter in the same beaker with the metal; add 20 c.c. 1.20 nitric acid; heat below boiling until the copper is dissolved; filter off the pulp; wash it forty times with water containing a little 1.20 nitric acid; evaporate the filtrate and washings to 20 c.c. in a 600 c.c. beaker and titrate the copper with cyanide and "silver nitrate." *Hold the copper solution about one hour after discharging the blue with cyanide and before titrating with the cyanide and silver nitrate.*

The author found that owing to the slowness of the reaction between the KCN standard and the copper ammonium compound that the above precaution of holding the solution for an hour after discharging the blue of the copper, and then, after the said interval, determining the excess of cyanide in the manner given on page 215, (*b*) and (*c*), is an essential one. It gives such satisfactory results that he prefers this volumetric method for the determination of copper. As the chemist usually has several titrations of copper to make, at the same time, no delay of any consequence results, as a number of tests can be given the first part of the titration for the discharge of the blue color, and, by the time the blue has been discharged from the last test, the first one has been standing the required time. It can then be at once finished with the cyanide and silver nitrate. The author now uses and recommends one-half the strength of cyanide standard given on page 214, that is, 1. c.c. equals 0.003175 gram of copper.

THE DETERMINATION OF OXYGEN IN COPPER

Gravimetric.—Burn off any grease adhering to the plate or bar, at a black heat. Pickle off any scale or film of oxide by dipping the sample in 1.20 nitric acid. Wash the sample after pickling, thoroughly, in distilled water. Dry the plate or bar at 100° C.

When drilling or milling the sample, use only bright new drills or milling cutters. Keep the drillings or millings in a desiccator filled with fresh anhydrous calcium chloride. To get a blank, run through the same apparatus as used for oxygen in steel, copper of known oxygen content, or else put through the apparatus copper that has been already freed from oxygen by putting it through the entire furnace reduction as given for steel in oxygen determination. See pages 81-87. When the blank from such oxygen freed copper is constant, then the apparatus is ready for the analysis of the sample to be tested.

obtained as in (*c*). The precipitates were then removed by filtration through double filters, and the excess of cyanide was determined in the filtrate and washings in the usual way with silver nitrate. The precipitates had to be poured through the filters several times to secure clear filtrates. The precipitates were washed ten times with dilute sodium carbonate water.

When titrating copper in the presence of 0.200 gram of bismuth the disappearance of the blue was taken as the end-point, as the basic bismuth clouded the solution. With but 0.100 gram of bismuth in solution the entire titration, as outlined in (*b*), was successfully carried through before the solution was perceptibly clouded.

Large quantities of manganese interfere with the titration of copper only in so far as dark-colored solutions are formed when the cyanide is added, thereby obscuring somewhat the end-point between the cyanide and the "silver nitrate." More citric acid is required. Add to the standardization about as much manganese as there is likely to be in the copper that is to be assayed. Use at least 6 grams of citric acid per 0.200 gram of Mn.

PRECIPITATION BY ALUMINUM

When using this well-known method one can proceed as at first described until the filtrate and washings from the lead sulphate are obtained. Evaporate the former to 20 c.c.; add 10 c.c. 1 : 3 sulphuric acid and a piece of aluminum $1\frac{1}{2}$ inches square by $\frac{1}{16}$ inch thick. Heat nearly to boiling for thirty minutes, or until the solution is colorless. Remove the aluminum and decant the solution through a 9 cm. filter; wash the filter fifteen times with water containing a few drops of 1 : 3 H_2SO_4. Return the filter to the 150 c.c. beaker in which the precipitation was made.

The filtrate and washings from the metallic copper should be tested with H_2S and, if a brown coloration is obtained, continue to pass the gas until the small precipitate of copper collects. Filter it out; wash it with H_2S water containing a drop or two of 1 : 3 H_2SO_4. Put this filter in the same beaker with the metal; add 20 c.c. 1.20 nitric acid; heat below boiling until the copper is dissolved; filter off the pulp; wash it forty times with water containing a little 1.20 nitric acid; evaporate the filtrate

CHAPTER IX

PART I

THE RAPID DETERMINATION OF NICKEL IN THE PRESENCE OF CHROMIUM, IRON AND MANGANESE

IN applying the method of T. Moore † to the determination of nickel in steel, the directions given on page 183, Analysis of Steel Works Materials by Brearley and Ibbotson, were followed: One gram of steel was dissolved in a 150 c.c. beaker with 10 c.c. of concentrated hydrochloric acid diluted with an equal volume of water.

When action ceased 10 c.c. of nitric acid (1.20) were added, and the contents of the beaker were boiled to about one-half. 16 c.c. of dilute sulphuric acid were poured into the solution and also 3 grams of powdered citric acid. The solution was stirred until the citric acid was dissolved, transferred to a 600 c.c. beaker, and rendered faintly but distinctly ammoniacal.

NOTE.—For Brunck's Dimethylglyoxime Method for Nickel and the author's modification of this separation, see page 231.

The nickel was titrated with a standard solution of potassium cyanide, using a measured amount of standard silver nitrate and 2 c.c. of a 20 per cent solution of potassium iodide as an indicator. The deep red color of the citrate of iron greatly obscures the end-point. The authors complain of this color and recommend the use of a condensing lens to cast a beam of light through the darkness. In the presence of chromium the writer found that a still more somber gloom settled down over the close of the reaction. The authors mentioned also state that this element retards the union of the cyanide and the nickel, causing the recurrence of the cloud of silver iodide.

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† Chemical News, 72, 92.

After struggling with the process for some time and always carefully separating the chromium, and with it the iron, in chrome steels, an attempt was made to dispel the darkness and also to avoid these tedious separations: Less citric acid per gram of steel was taken, and the dark red shaded to blackness.

Naturally, the amount of citric acid per gram of steel was then increased, that is, 6 grams of citric acid per gram of steel were used, and a marked improvement was noted. Still more citric acid caused a complete lifting of the shadows.

The following modified procedure was finally adopted for nickel steels after having been thoroughly tested with plain carbon steels to which known amounts of nickel had been added: Dissolve 1 gram of steel drillings in a 150 c.c. beaker with 20 c.c. of hydrochloric acid (1 : 1). When action ceases add 10 c.c. of nitric acid (1.20).

Reduce the volume of the solution to about 15 c.c., keeping the beaker covered during the boiling. Remove the beaker from the fire and pour into it 8 c.c. of conc. sulphuric acid diluted with 24 c.c. of water. The presence of the sulphuric acid is essential to a sharp end reaction between the cyanide standard and the silver iodide in the subsequent titration.

Transfer the contents of the beaker to one of 600 c.c. capacity containing *twelve* grams of powdered citric acid. Stir until the citric acid is dissolved. Render this solution *faintly* but *distinctly* alkaline with ammonia, using one part of concentrated ammonia diluted with one part of water. A large excess of ammonia causes low results. Stand the beaker in running water until it is cold. The volume of the solution should now be about 300 c.c. Much larger volumes than 300 c.c. should be avoided, as great dilution retards the end-point, causing the cloud of silver iodide to disappear and then to reappear again in a few minutes.

The faintly ammoniacal condition * can be easily controlled by adding the ammonia rather slowly and noting the changes of color that ensue: The first change is to amber, then to yellowish green, then to distinct green, then to a light shade of green, then to a yellow almost matching the yellow color of the acid solution. The reappearance of the yellow tint indicates that alkalinity is nearly attained.

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* One can, also, use litmus paper; add ammonia, drop by drop, until 1 drop of 1 : 1 ammonia just turns the red litmus blue, then add 10 drops excess of the ammonia and no more. A person with the average sense of smell can add ammonia until a slight sweet smell is obtained and then the 10 drops of excess with better success than with the use of litmus.

A little more ammonia now causes a brownish shade, which is evidence that the ammonia is in slight excess. The moderately alkaline citrate of iron obtained in the proportion of 1 gram of iron to 12 grams of the citric acid yields a bright greenish yellow solution in plain nickel steels instead of being of a dense dark red shade.

To the cold solution 2 c.c. of a 20 per cent solution of potassium iodide are added. From a 50 c.c. burette a standard solution of silver nitrate is dropped into the same beaker, producing with the iodide a white turbidity. The standard potassium cyanide is added with constant stirring until the cloud of silver iodide just disappears, which it does on being converted into silver cyanide. Nickel cyanide is first formed, and then the silver cyanide is produced:

$$(1)\quad \mathrm{Ni(NO_3)_2 + 4KCN = Ni(CN)_2 \cdot 2KCN + 2KNO_3}.$$

$$(2)\quad \mathrm{AgNO_3 + 2KCN = AgCN \cdot KCN + KNO_3}.$$

If the directions are followed as given, the titration can be accomplished at almost the full speed of the burette. If the titrated solutions are permitted to remain in the open beakers for a time, a film usually appears on the surface of the liquid. No account is taken of it, as its presence is most likely due to a superficial loss of ammonia. The reactions are always found to be completed when the body of the solution is freed of the iodide precipitate.

Standards.—From the equations as given, 5.85 grams of silver nitrate are equivalent to 4.4868 grams of potassium cyanide. This weight of cyanide dissolved in 1 liter of water gives a value of 1 c.c. equals about 0.001014 gram of nickel.

As comparatively little silver nitrate is needed with each analysis, it is not advisable to prepare more than a half liter of the water solution of this salt, using 2.925 grams per 500 c.c. of distilled water.

The potassium cyanide standard should contain about 5 grams of potassium hydroxide to the liter which renders it quite permanent. The solutions are readily standardized by applying them to a plain steel to which a known amount of nickel has been added. The chemically pure double sulphate of nickel and ammonium is a convenient standardizing medium. For example, 0.2 gram and 0.25 gram of the double sulphate can be weighed into 150 c.c. beakers together with 1 gram of plain carbon steel drillings.

This mixture is then put through all of the foregoing manipulations and titrated with the cyanide solution that is to be standardized. The number of c.c. of the silver nitrate and of the potassium cyanide solution used in this titration are noted. An excess of 10 c.c. of the cyanide is now added and in turn titrated with the silver nitrate solution until a distinct cloud of silver iodide is produced. This second titration gives the relation between the silver solution and the cyanide.

An actual case will illustrate the calculations: In sample No. 3477, 1.7 c.c. of standard silver nitrate solution were required to produce a distinct turbidity and also to combine with any excess of potassium cyanide standard. In all, 35 c.c. of the cyanide were consumed in the titration. When the cloud of silver iodide had just been dispelled, an excess of 9.8 c.c. of cyanide was allowed to flow into the clear solution. Just 10.1 c.c. of silver nitrate standard were needed to produce a reappearance of the cloudiness. Therefore $9.8 \div 10.1 = 0.97$, or 0.97 c.c. of cyanide standard solution equals 1 c.c. of silver nitrate. Hence instead of deducting 1.7 c.c. from 35 c.c., 1.7×0.97 or 1.65 c.c. were deducted, leaving 33.35 c.c. of cyanide combined with the nickel in this steel.

To a plain carbon steel 0.200 gram of double sulphate of nickel and ammonium were added put through all of the steps of a regular analysis. This mixture required 28.75 c.c. of cyanide. The nickel salt contains 14.86 per cent of nickel, or $0.200 \times 0.1486 = 0.02972$ gram of nickel were present. Hence $0.02972 \div 28.75 = 0.00103$, or 1 c.c. of standard cyanide solution is equivalent to 0.00103 gram of nickel. No. 3477, as has been stated, required 33.35 c.c. of the cyanide standard, and therefore contains $0.00103 \times 33.35 = 0.03435$, or 0.03435 gram of nickel, or 3.435 per cent.

CHROMIUM-NICKEL STEELS

When chromium is present proceed exactly as in plain nickel steels except that 24 grams of citric acid per gram of steel are used. This proportion of citric acid is adequate to render the end-point quite as easy to see as in ordinary nickel steels. The action is prompt and free from recurrence of turbidity. Of course, cloudiness through the entire solution will occur, as the ammonia is dissipated from it, after it has stood for some time in an open beaker.

The tabulation (1) that follows furnishes satisfactory proof that chromium does not interfere with the successful technical estimation of nickel in its presence:

TABLE I

Sample.	No Chromium Added Nickel Found, Per Cent.	Per Cent of Chromium Added to a Portion of the Same Steels	Nickel Found after the Addition of Varying Amounts of Chromium.
Number			
525	5.09	4	5.10
2991	4.44	2	4.45
7239	3.24	1	3.28
3017	4.96	1	5.03
612	3.47	0.5	3.47
7273	3.29	1	3.31
622	3.56	0.5	3.56
7288	3.32	2	3.41
7289	3.11	2	3.16
663	3.57	6	3.59
2991	4.44	3	4.47

The chromium was introduced in the form of recrystallized chemically pure potassium dichromate. The dichromate crystals were mixed with a weighed amount of nickel steel drillings before the addition of the 20 c.c. of hydrochloric acid. The combined action of the nascent hydrogen from the steel, the excess of boiling hydrochloric acid and the ferrous chloride reduced the chromate to chromic chloride, thus duplicating the conditions found when a chromium-nickel is similarly treated.

Determination by this modification of the cyanide method can be finished in from forty-five to fifty minutes, either in the presence or absence of any per cent of chromium likely to be met with in steels or alloys soluble in the acids given. In this laboratory *duplicate* determinations in nickel or nickel-chromium steels are made in the time just specified. By the process one can decide in a few minutes whether or not nickel is present in a given steel and just how much. Tungsten, if present, does not interfere, appreciably, as has been noted by the authors mentioned in this article. The writer had two different amounts of nickel added to a steel containing several per cent of chromium and from 16 to 17 per cent of tungsten. This steel was then carried through exactly as though no tungsten or chromium were present, using the method as given for chromium-nickel steels.

Nickel Added, Gram	Nickel Found Gram
0.0297	0.0299
0.03715	0.0372
None	0.0006

Table II demonstrates that neither vanadium, tungsten, chromium, nor molybdenum, when present, in the amounts given, interfere appreciably in technical analysis. These amounts represent extreme cases, especially for the vanadium, it being equivalent in one instance to 3.5 per cent V when 1 gram of steel is taken.

Tests were then made in the same manner in the presence of molybdenum and vanadium as follows:

TABLE II

Name	Kind of Steel or Mixture	Nickel Added, Gram	Nickel Found, Gram
J. R. steel	Contains 10% ±Mo	0.0297	0.0295
J. R. steel	Contains 10% ±Mo	0.0222	0.0223
J. R. steel	Contains 10% ±Mo	None	0.0002
Bxx–173 steel	Contains 4% Mo and 4% Cr.	0.0223	0.0222
Bxx–173 steel	Contains 4% Mo and 4% Cr.	0.0297	0.0296
Bxx–173 steel	Contains 4% Mo and 4% Cr.	None	0.0004
A mixture	0.920 gram of steel	0.0297	0.0298
	0.030 gram of nickel	....	.....
....	0.018 gram of vanadium	....	......
A mixture	0.840 gram of steel	0.0223	0.0227
....	0.022 gram of nickel		......
....	0.035 gram of vanadium		.
A blank	1.000 gram of steel	None	0.0008
....	0.035 gram of vanadium	..	....

As copper also forms cyanides, its presence would cause results to be too high, but copper is avoided in good steel making. Its presence is unlikely in greater amounts than 0.06 per cent, although the writer, on one occasion, found as much as 0.25 per cent in a low carbon steel, not a *crucible* steel, however. Crucible steel rarely contains over 0.04 per cent copper. The choice brands are under 0.03 per cent in copper.

Wishing to test the extent to which nickel could be titrated in the presence of large percentages of chromium, iron being also present, the mixtures as given in Table III were titrated with potassium cyanide. The various salts were weighed into 150 c.c. beakers, together with the proper amounts of steel drillings. The same proportions of hydrochloric, nitric, citric and sulphuric acids were employed as are herein given for nickel-chromium-steels, and were applied in the same manner.

A sufficient quantity of the salts of chromium and nickel, and of the steel drillings, were taken to give a total of one-half gram of metals in the mixture.

Double sulphate of nickel and ammonium ($(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6H_2O$), potassium dichromate and steel drillings free from nickel were used as sources of nickel, chromium and iron, respectively.

To obtain the nickel value of the cyanide standard under conditions similar to those existing in the mixtures tested, standardizing mixtures of these salts were prepared varying from the mixtures tested as much as 1 per cent to 20 per cent in the different constituents.

TABLE III

Per Cent of Metals			Gram of Nickel	
Ni	Cr	Fe	Added	Found
30	40	30	0.1499	0.1494; 0.1495
60	20	20	0.2999	0.3003; 0.2989
20	40	40	0.1029	0.1022
5	90	5	0.0250	0.0248; 0.0244
4	92	4	0.0200	0.0199
1.5	95	3.5	0.00749	0.00805; 0.00822
0.5	99	0.5	0.00249	0.00225; 0.00243 0.00247; 0.0026
0	98.9	1.0	None	None

For mixtures exceeding 10 per cent of nickel a standard cyanide solution with a nickel value of 1 c.c. = 0.0031 gram of nickel was used. The standardizing mixtures were dissolved and treated exactly as the mixtures tested. The same method of standardization was observed in the work recorded in Table IV.

Table III demonstrates that nickel may be estimated by the foregoing modified cyanide process, using the proportions of citric acid as given, with sufficient accuracy for works analysis, and indeed for most practical purposes, even when the percentage of chromium is as much as 99 per cent, and the nickel content is but one-half of 1 per cent.

* The titration of the mixtures given in Table III, and containing the larger amounts of chromium, requires considerable practice on the part of the operator. The work should always be carried out in duplicate. The disappearance of the cloudiness in the presence of 0.100 to 0.450 gram of chromium in a volume of 350 to 400 c.c. is much more exactly observed when the mixture containing the iodide cloud is compared, from time to time, with a *similar* mixture which is perfectly free of this milky turbidity. The dilution of the deep purple, or wine color, of these ammoniacal mixtures of citrates to more than 300 to 400 c.c. renders the end-point but slightly more distinct, and has the great objection of retarding the reaction between the cyanide and the nickel. The increase above 24 grams of citric acid, in the solution, even to the extent of adding 60 grams of citric acid, did not relieve the density of color to any perceptible extent.

When titrating with a standard, 1 c.c. of cyanide = 0.0031 gram of nickel (three times the strength used for steels), do not also increase the strength of the silver standard to equal it, but still retain the silver nitrate standard as given for steels. A silver nitrate solution sufficiently concentrated to be equivalent, volume for volume, to the cyanide standard (1 c.c. = 0.0031 gram of nickel) on being dropped into the solution containing the potassium iodide, does not produce the usual opalescence, alone, but forms curds of iodide that do not readily combine with the cyanide standard. The end-point is reached and the main body of the solution is free of cloud while curds of silver iodide still lie on the bottom of the beaker. The weaker silver nitrate standard, or 5.85 grams of silver nitrate to the liter, produces with the potassium iodide a finely divided cloud of precipitate that combines promptly with the strong cyanide standard, giving a sharp end-point. Weigh, therefore, 2.925 grams of silver nitrate, diluting to 500 c.c., and 13.4604 grams of the best grade of potassium cyanide, diluting to 1000 c.c., for titrations of solutions containing from 0.100 to 0.300 gram of nickel; 1 c.c. of this silver nitrate solution should be equivalent to $\frac{1}{3}$ c.c. of the concentrated cyanide standard (1 c.c. cyanide = 0.0031 ± grams of nickel).

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* Read the determination of nickel in the presence of much chromium, page 229.

The titration of nickel by potassium cyanide in mixtures containing large percentages of manganese with varying amounts of chromium and iron was also tried.

As in the experiments outlined in Table III, mixtures were prepared to contain one-half gram of metallic substances. The same nickel and chromium salts were employed. Potassium permanganate crystals supplied the manganese.

The crystals of double sulphate of nickel and ammonium, potassium dichromate and potassium permanganate were weighed into a 150 c.c. beaker with the steel drillings. To this were added 20 c.c. of dilute hydrochloric acid. The contents of the beaker were then boiled, after the first action was completed, until the chromate and permanganate were reduced. An addition of 10 c.c. of nitric acid (1.20) followed, and the analysis was carried out exactly as given for chromium-nickel steels, using 24 grams of citric acid. The results obtained are given in Table IV. Sulphuric acid was added as in the process for steels.

Table IV gives evidence of the fact that nickel can be accurately determined in the presence of large percentages of chromium and manganese, if the conditions herein given are carefully observed. In the hands of a practiced operator no difficulty was experienced in the analysis when as much as 95 per cent of manganese was in solution with but 0.25 per cent of nickel.

Where large amounts of reduced chromium are encountered with nickel, the latter can be titrated to a better advantage by boiling the sulphuric acid solution of the sample with an excess of $KMnO_4$; filtering out the manganese oxide and then proceeding with the addition of the citric acid, etc., (see E. D. Campbell and W. Arthur, J. Am. Chem. Soc., 30, 1116–20, July, 1908).

TABLE IV

Per Cent of Metals				Gram of Nickel	
Ni	Mn	Cr	Fe	Added	Found.
41	20	10	30	0 2059	0 2058
20 6	40	20	20	0 1029	0 10228
15	60	15	10	0 0750	0 0752
1.5	95 5	1	2	0 00749	0 00762
0.25	94 9	2	2.9	0 00124	0 00122
....	94 9	2	4	None	0 00006

'here is not the slightest need for all this extra work for any mount of chromium ever found in steels, unless it is desired to etermine this element in the same analysis with the nickel. n that event use 4 grams of steel and proceed as in CrV steels 'hapter II); and, when the solution is ready for the titrations, *ivide it in two equal portions.* Finish one portion for Cr and V y the method in Chapter II. Finish ONE-HALF of the other art for nickel, adding citric acid, etc. This procedure avoids ıe reoxidizing and refiltering resorted to by Messrs. Campbell nd Arthur; and also any necessity of making the objectionable ɔot tests. It affords an easy way of getting Cr, V, and Ni from ıe one analysis.

Add the citric acid after neutralizing the free acid when large mounts of chromium or vanadium are present with the nickel.

By first performing the neutralization before adding the citric ɔid, the latter is prevented from reducing the vanadium or ıromium and, in this way, the intense dark colors are elimiated. It is still better to not only neutralize the free acid of ıe chromic acid-nickel or the vanadic acid-nickel solution, but to so convert the citric acid to ammonium citrate before adding ıis organic compound to the almost or entirely neutral solution the nickel and chrome, or nickel and vanadium. This of ɔurse applies only to the filtrate after boiling with permanganate oxidize the vanadium to the vanadic and the chromium to ıe chromic state. This oxidation is highly to be recommended hen large amounts of vanadium or chromium are present.

After adding the ammonium citrate, the usual amount of cess of ammonia is introduced and the citrate will gradually ssolve the iron hydroxide after prolonged stirring.

THE COMPLETE ANALYSIS OF "30 PER CENT" NICKEL STEEL

Iron.—Dissolve 0,3 or 0.45 gram of sample in 30 c.c. of 1.20 nitric acid in a porcelain dish, and when the action is over, evaporate the solution to dryness; ignite the bottom of the dish to a dull red to destroy the carbon; cool; dissolve in 20 c.c. of conc. HCl and finish as in iron ore by reduction with stannous chloride and titration with potassium dichromate standard. The nickel does not interfere except to turn the spot tests cloudy, but not so quickly but that the end-point can be seen. 0.45 gram of sample required 53.2 c.c. of the standard; 53.2 times 0.00565 divided by 0.45 times 100 equals 66.7 per cent iron.

Standardization in the Presence of Nickel.—Dissolve 0.300 gram of the U. S. Bureau Sibley iron ore together with 1.00 gram of double sulphate of nickel and ammonia, as above, and put it through all of the operations as given. Titrate it with the regular dichromate standard as used for iron ore (9.8 grams of recrystallized $K_2Cr_2O_7$ dissolved in water and diluted to 2000 c.c.). This gives a factor of 1 c.c. equals 0.00565 gram of iron, that is, 36.7 c.c. of the standard were used, hence 0.300 times 0.692 divided by 36.7 equals 0.00565.

The carbon, manganese, etc., were determined as in plain steels.

RESULTS

	Per Cent		Per Cent
Carbon	0 20	Silicon	0 125
Manganese	0 74	Nickel	32 27
Phosphorus	0 025	Iron	66 75
Sulphur	0.025		

BRUNCK'S METHOD FOR NICKEL IN STEEL

This method is supposed to separate nickel from iron, chromium, zinc, manganese and cobalt. The presence of a large quantity of manganese requires the precipitation to be made from acetic solution. The procedure for steel is to dissolve from 0.5 to 0.6 gram in 10 c.c. of 1 : 1 HCl with heat. Oxidize with nitric acid; boil off the red fumes; silicon is not removed; it would seem to the writer that it would be safer in some steels to remove the silicon by evaporation to dryness.

Add from 2 to 3 grams of citric acid and make the solution slightly ammoniacal to see if any precipitation occurs. If the solution remains clear, add HCl drop by drop until slight acidity is attained. Heat to near boiling; add 20 c.c. of a 1 per cent solution of dimethylglyoxim in alcohol. Now drop in ammonia to slight alkalinity. Let stand for one hour and filter hot. Wash with water. The red precipitate is caught on a Gooch or Munroe crucible and, after being thoroughly washed, is dried for forty-five minutes at from 110° to 120° C. The weight obtained is multiplied by 0.20326 to convert it to metallic nickel which is then calculated to percentage.

The percentage of 20.326 corresponds to the formula of $C_8H_{14}N_4O_4Ni$. Prettner recommended the holding of the solution for an hour before filtering off the scarlet precipitate. Those wishing to read the original descriptions of the method should consult Zeitschrift für Angew. Chemie, 1907, Nr. 47, S. 1844. Dr. O. Brunck. Also Chem. Ztg., 33, 1909, p. 396.

A MODIFICATION OF BRUNCK'S METHOD BY SOLUTION OF THE RED PRECIPITATE IN NITRIC ACID AND TITRATION OF THE SOLUTION IN THE USUAL WAY WITH KCN AND SILVER NITRATE

Proceed as for nickel as in Brunck's method, obtaining the red precipitate, which is washed fifteen times with 500 c.c. of water containing 10 c.c. of a 2 per cent solution of the dimethyl. The precipitate is dissolved off the filter with 25 c.c. of 1.20 nitric acid, allowing the solution to run into the beaker in which the precipitation of the nickel was made. Wash the filter about thirty times with water containing 10 c.c. of 1.20 nitric acid per 500 c.c. of water, or until the wash water no longer gives a test for nickel with the dimethyl. Add 15 c.c. of 1 : 3 sulphuric acid to the nitric acid solution of the red precipitate; boil twenty minutes; cool; add 5 grams of citric acid; make faintly ammoniacal; add 10 drops of 1 : 1 ammonia and finish for nickel by titration with KCN and silver nitrate. By this method the U. S. nickel-chrome standard, No. 32 (1.62 per cent Ni) gave

1.63 per cent nickel, and the U. S. nickel standard No. 33 (3.33 per cent Ni) gave 3.36 per cent Ni.

One should be able to use this method for the determination of small amounts of nickel by taking large weights of the sample. Elements like manganese, vanadium, and chromium, that give very dense dark citrates when in the "ous" state, could be analyzed for small per cents of nickel in the above manner by separating away the bulk of these elements from the nickel. (See the Determination of Small Amounts of Nickel in the Presence of Large Amounts of Cobalt, page 382.) The idea of such a modification of Brunck's method was suggested to the author by Mr. A. G. Greenameyer. The above details are the author's.

For the Determination of Nickel by Electrolysis, see page 386.

THE PRESENT ROUTINE STANDARD METHOD FOR NICKEL (May, 1919)

Nickel in Steel.—Weigh 1 gram of the sample into a clean 400 c.c. beaker. Add 25 c.c. nitric acid (sp. gr. 1.20); put cover glass on beaker and place on argand stove over a low flame until sample is dissolved. Add 15 c.c. sulphuric acid (1 : 3); raise flame slightly and *boil until all brown fumes have been driven off.* Failure to entirely expel the brown fumes causes inaccurate results. Remove from stove; rinse cover glass and sides of beaker with distilled water. Allow to cool somewhat; then add 10 grams citric acid (powdered).

Add 50 to 60 c.c. ammonia water (1 : 1); stir until citric acid crystals are in solution; then transfer beaker to a pan of cold water. (Do not float the beaker, it may upset.) If the solution when cold still smells strongly of ammonia, add 1 : 3 H_2SO_4 a few drops at a time or until the test smells only slightly ammoniacal. However, if when cooled, solution instead of being ammoniacal is neutral or faintly acid, turning blue litmus to a red, then add *ammonia* a few drops at a time until the solution is faintly ammoniacal.

The test is ready for titration when it has a distinct, but not strong smell of ammonia. At this stage, red litmus turns blue where it dips into the solution. If the solution is strongly ammoniacal. low results are obtained. If it is too faintly ammoniacal high results are gotten. The operator soon learns to judge the right amount of ammonia.

To the faintly ammoniacal solution, add 2 c.c. of potassium iodide from a small graduate and stir. Using a burette containing silver nitrate solution, note the reading of the burette; then add ·2 c.c. of the same to the test and stir well. A pale yellow cloud should form throughout the solution.

Using another burette containing dilute standard potassium cyanide solution, note the reading, then add just enough of this solution to clear up the cloud that was previously formed—thus finally obtaining a clear solution. Stir constantly during the addition of the KCN.

Record the final readings of both silver nitrate and potassium cyanide burettes. By subtraction the number of c.c. consumed, of each are obtained.

STEELS CONTAINING CHROMIUM

Dissolve first in a mixture of 30 c.c. of H_2SO_4 (1 : 3) and 20 c.c. distilled water. Heat until dissolved, oxidize with 20 c.c. HNO_3 (1.20). Boil off all brown fumes; remove from fire; cool; add the citric acid and proceed as given above.

CALCULATIONS

Known Mixture for Standardizing

200 mg. NiAm sulphate (14.8% Ni) — Place in 400 c.c. beaker and run
1 gm. plain steel — simultaneously with tests
(Most steels contain at least 0.02% Ni and 0.025% Cu.)

14.0 c.c.	Final Reading	82.3 c.c.
12.0 c.c.	Start	49.6 c.c.
2.0 c.c. total silver nitrate	Total cyanide	32.7 c.c.
1.1 c.c. (1 c.c. silver = 1.1 c.c. cyanide)	Silver equivalent..	2.2. c.c.
2.2. = silver nitrate used by the excess of KCN.	Nickel equivalent.	30.5 c.c.

14.8% Ni in Nickel Ammonium Sulphate.
.2 gram
30.5)2.9600(0.097 or 1 c.c., = 0.00097 gram Ni

Factor 1 c.c. cyanide, 0.097 per cent Ni on 1 gram basis.

High Nickel Steels

Run as directed above, but use conc. KCN solution for titration. 1 c.c. $AgNO_3$ usually equals 0.226 c.c. strong KCN.

CAUTION.—Be extremely careful in handling cyanides, as they are very poisonous.

Keep silver nitrate solution away from bright light, especially sunlight, which causes it to undergo decomposition.

CHAPTER IX

PART II

THE ANALYSIS OF NICKEL-CHROMIUM ALLOY

THE widespread application of true nickel-chromium and nickel-chromium-iron alloys to resistance heating has made further work for the analyst.

The author has analyzed several varieties of these useful alloys as follows:

NICKEL

Dissolve 0.5 gram of the wire in a No. 5 porcelain dish with a mixture of 20 c.c. conc. HCl and the same amount of conc. HNO_3 and evaporate to 15 c.c. Add 100 c.c. of conc. HNO_3 and evaporate to 20 c.c. Transfer the solution to a 600 c.c. beaker; add 40 c.c. of 1 : 3 H_2SO_4; dilute to 200 c.c.; heat to boiling; add permanganate of potassium to the boiling solution until an excess of brown manganese oxide remains without perceptible change after a half hour of boiling; cool; filter on an asbestos plug or through a porous crucible, making sure that none of the manganese oxide runs through, as the filtrate must be perfectly clear. Cool; add 1 : 1 ammonia until a precipitate starts to form; add 15 grams of citric acid made slightly alkaline to litmus paper by ammonia. Add ten drops more of the ammonia, if necessary to render the solution slightly alkaline. Titrate the solution with the concentrated KCN standard given on page 227. To standardize the cyanide under conditions similar to the alloy, put the following mixtures through all of the above operations and then titrate them with the KCN: Mixture No. 1, 1 gram of the nickel-ammonium sulphate, and 200 mgs. of potassium dichromate; mixture No. 2, 2 grams of nickel-ammonium sulphate and 200 mgs. of the dichromate. The nickel-ammonium sulphate used in this work was checked by electrolysis and found to contain 14.6 per cent nickel, hence mixture No. 1 contained 0.146×1.00 or 0.146 gram of nickel, and mixture No. 2 contained 0.146×2.00 or 0.292 gram of nickel.

CHROMIUM

Dissolve 0.500 gram of the finely ground sample exactly as given for nickel and proceed with the analysis as for nickel and filter off the excess of manganese oxide as in the case of the nickel. Cool the filtrate if the titration is to be finished forthwith; omit the neutralization with ammonia; and titrate, after adding 40 c.c. of 1 : 3 sulphuric acid and diluting further to 250 c.c. with water. Titrate with the same strength of sulphate and permanganate standards as are given on pages 12 and 13. Do not use any ferricyanide indicator, as the nickel would be precipitated and hide the end-point. First add the sulphate standard until all red tints are gone and there remains only the chrome green; then add an apparent excess of about 10 c.c. Next titrate with the equivalent permanganate standard until a faint permanent pink flush is visible through the green of the chromium. The amount of the sulphate used less the number of c.c. of the permanganate required to produce the pink end-point is multiplied by the value of the double sulphate in chromium per c.c. The result equals the number of milligrams of chromium in the 0.500 gram of sample. The standardization is accomplished by putting the following known mixture through all of the foregoing operations: 0.250 gram of plain carbon steel, 0.100 gram of recrystallized potassium dichromate and 2 grams of nickel-ammonium sulphate; also the same amounts of steel and nickel salt with 0.200 gram of the dichromate. These mixtures are titrated in the same way as described for the sample itself and the value of the sulphate in chromium is calculated in the usual way. The value of the dichromate in metallic chromium is taken as 35.35 per cent Cr.

MANGANESE

Dissolve 0.300 gram of the wire in a mixture of 10 c.c. of conc. nitric acid and 5 c.c. of conc. hydrochloric acid. Evaporate to 5.0 c.c.; add 50 c.c. of conc. nitric acid and evaporate to 10 c.c.;

add 25 c.c. more of the nitric acid and again evaporate to 10 c.c. Transfer to a 10×1 inch tube and finish as in chrome steels, as directed on page 32.

CARBON

Twist several strands of the wire into a rope and take millings therefrom as described under Milling (see page 271). Then burn with red lead as in ferro-chromium

SULPHUR AND SILICON

The sulphur is determined as in the gravimetric method for alloy steels. The silicon is obtained from the insoluble matter filtered out before precipitating the sulphur with barium chloride.

IRON AND ALUMINUM

Dissolve 1 gram of millings in a mixture of 20 c.c. of conc. HCl and 20 c.c. of conc. HNO_3. Heat until all action is over; boil down to 20 c.c.; transfer to a liter boiling flask; dilute to 300 c.c. and peroxidize, as described on page 35, getting filtrates A and B, and if B has a distinct yellow color, then a third peroxidation should be made, obtaining a third filtrate and washings C that are free from an appreciable yellow color, showing that all of the chromium has been separated from the iron present. The aluminum is obtained from A, B and C, as in ferro-vanadium, that is, by adding 1 : 1 HCl slowly with *constant* stirring until turmeric paper is no longer *immediately* turned to even a suggestion of a brownish red color on being dipped into the solution. The operator can easily tell when he is approaching the end-point by the sudden increase of the effervescence, as the acid is added; also if aluminum is present to the extent of even 1 per cent the solution will have become cloudy and if several per cents are present, the usual white, flocculent, precipitate of aluminum hydroxide will have formed. Continue to add the acid until the turmeric shows no more immediate change of color than if it had been dipped into water. Of course in a minute or two the paper will take on a faint brownish red. At this stage the solution will change litmus paper at once to a distinct blue. A, B and C can be combined in one before performing the precipitation of the aluminum, or if the volumes are too great they can be treated separately and the precipitates combined on the one filter. The alkaline solution is brought just to a boil, before adding the acid, but in no case should the strongly alkaline solution be heated further, as by so doing large amounts of glass are dissolved. The precipitate of aluminum is then washed and dissolved off the filter, reprecipitated with a slight excess of ammonia and weighed as Al_2O_3 plus a little P_2O_5 and SiO_2 and finished from that point on as given on page 36 and on page 37.

The Iron.—All of the iron will be on the filter from filtrate C, except a slight film which will be clinging to the walls of the boiling flask. The latter is cleaned by warming in the flask a little 1 : 1 HCl and the iron on the filter is dissolved off with hot acid of the same kind. The iron from the flask and the filter are combined and titrated as in iron ore after reduction with stannous chloride. To standardize the dichromate the following known mixture was put through all of the foregoing operations: 250 mgs. of standard iron ore, 0.100 gram of potassium dichromate and 2.00 grams of the nickel-ammonium sulphate. Also for a check, 0.260 gram of the iron ore, and the same amounts of the other two salts as before. The Sibley ore No. 27 of the U. S. Bureau of Standards is extremely useful as a known source of iron to add to all such standardizing mixtures. The salts of nickel and chromium are of course added to have the standardizing mixtures as near the samples as possible.

SOME TYPES OF NICKEL-CHROMIUM AND NICKEL-CHROMIUM-IRON ALLOYS

	No. 1	No. 2	No. 3	No. 4	No. 5
Carbon	0.12	0.35	0.30	0.14	0.41
Manganese	0.82	2.74	1.50	Trace	1.95
Sulphur	0.012	0.074		0.027	0.026
Nickel	76.93	60.35	66.42	83.91	56.47
Chromium	16.40	10.12	19.37	13.97	15.64
Silicon	0.23	0.40	.		1.66
Iron	1.81	25.11	10.23	1.47	22.58
Aluminum	2.68	0.53	.....	....	1.20
Phosphorus	....	...	...	...	0.03

CHAPTER IX

PART III

THE ANALYSIS OF NICKEL-COPPER IRON ALLOY (MONEL METAL)

SILICON AND COPPER

DISSOLVE 0.5 or 0.6 gram of the drillings or millings in a No. 5 porcelain dish with 35 c.c. of 1.20 nitric acid. In the same manner dissolve two standardizing mixtures as follows: (1) 0.100 gram of 99.9 per cent metallic copper and 2.00 grams of the double sulphate of nickel and ammonia. (2) 0.200 gram of the copper and 3 grams of the double sulphate. Heat until all action with the nitric acid has ceased; add 70 c.c. of 1 : 3 sulphuric acid and evaporate to thick white fumes. Add 100 c.c. of water; heat until all is in solution except a little white insoluble residue of flotant silicic acid which is filtered through a double 11 c.c. ashless filter and washed free of iron with water containing 10 per cent by volume of 1 : 3 sulphuric acid. Finish the washing with water; get the silicon from the residue on the filter as in steels, page 348, by loss of weight after evaporation with a few drops of conc. sulphuric acid and 10 c.c. of hydrofluoric acid. Any residue of oxides remaining after this evaporation and ignition is dissolved out with a little conc. HCl and the solution is added to the main filtrate from the silicon. This filtrate is diluted to 400 c.c. with water, heated nearly to boiling, and hydrogen sulphide is passed through it until the copper separates out well. Filter the sulphide of copper through a double 12½ cm. filter and wash with H_2S water containing 5 drops of 1 : 3 sulphuric acid per 500 c.c. of water, giving not less than forty washings. Dry the filter, burn it off at a low red heat in a porcelain crucible, and dissolve the copper oxide in 20 c.c. of 1.20 nitric acid. Transfer the solution to a 400 c.c. beaker; add 1.5 grams of citric acid; make neutral with a saturated solution of sodium carbonate and add 25 c.c. excess of the carbonate. Titrate the copper by the cyanide method as described on pages 213 to 216. For the indicator use a 20 per cent KI solution (20 grams of the KI to 100 c.c. of water); for the cyanide use 4.4868 grams to the liter; and for the silver nitrate dissolve 2.925 grams in water and dilute to 1 liter. It may be well to give the routine of the titrations here. Add the KCN to the solutions containing the various amounts of test and the known mixtures until all blue color is gone; then wait at least a half hour before proceeding with the cyanide and silver titration. Unless this pause is made discordant results will be obtained, owing to the slowness of the complete reaction between the cyanide added to discharge the blue, and the copper. After the half to one hour interval, add 2 c.c. of the KI indicator, and then the silver nitrate until a slight white cloud of silver iodide appears that is permanent. To get the relation between the silver and the cyanide next add 5 c.c. of the KCN standard and again add the silver until the slight cloud again appears.

Standardization and Calculations.—Mixture No. 1 required 83.2 c.c. of the KCN to discharge the blue color, and after waiting for at least a half hour it required 6.5 c.c. of the $AgNO_3$ standard to produce a slight cloud of silver iodide in the solution; further, on adding an excess of the KCN of 5 c.c. it required 4.3 c.c. of the $AgNO_3$ to again produce a slight permanent cloud in No. 1. By this last titration, therefore, 4.3 c.c. of the "silver" equal 5.0 c.c. of the cyanide. Since 6.5 c.c. of the silver solution were needed to produce the first slight cloud after the thirty-minute delay, then 6.5×5 divided by 4.3 or 7.5 c.c. must be deducted from the 83.2 c.c. required to discharge the first blue in order to obtain the actual amount of the KCN standard that was used by the copper taken. This gives 75.7 c.c. of the KCN equal to 0.100×99.9 of metallic copper or 0.0999 gram, or 1 c.c. of the KCN equals 0.00132 gram of copper. In the same way from mixture No. 2 it was found that 149.8 c.c. of the KCN equal 0.1998 gram of copper, or 1 c.c. of the KCN equals 0.001333 gram of copper. The average of the two standardizations was 0.00133, In the same manner 0.5 and 0.6 gram of the monel gave 26.6 and 26.9 per cent copper.

NICKEL IN MONEL

The filtrates from the H_2S precipitation of the copper are evaporated to fumes with 100 c.c. of 1 : 3 H_2SO_4; cool; add 50 c.c. of water; and then 10 c.c. of conc. HNO_3; heat to destroy any remaining hydrogen sulphide; filter if not clear, and titrate with cyanide and silver. For the cyanide standard dissolve 44.868 grams of KCN in water and dilute to 2 liters, and for the silver nitrate and the potassium iodide use the same strength as given for the copper. In making the titration add 2 c.c. of the KI and then the $AgNO_3$ until a distinct white cloud of the silver iodide is formed; then add the KCN until the cloud just disappears; then add 10 c.c. excess of the KCN and just bring back the white cloud to get the relation between the silver nitrate and the KCN. As No. 1 (see copper) contained 2 grams of the nickel ammonium sulphate, there were present, theoretically, 0.1486×2.00, or 0.2972 gram of nickel. By the excess titration it was found that 1 c.c. of the $AgNO_3$ equals 0.21 c.c. of the KCN. The first cloud produced by the addition of the 2 c.c. of KI did not disappear until 61.0 c.c. of the KCN had been added. In the standardization 2.4 c.c. of the $AgNO_3$ were actually added to produce the cloud with the KI; and by the titration of the 10 c.c. of excess KCN, 47.6 c.c. of the $AgNO_3$ were required to again reproduce the cloud; therefore, 61.0 c.c. less 2.4×10 divided by 47.6, or less 0.504 c.c., equal 60.5 c.c. which equal 0.2972 gram of nickel, or 1 c.c. of the KCN equals 0.00491 gram of nickel. In the same way mixture No. 2 gave 1 c.c. of the KCN standard equals 0.00493 gram of nickel. From the 0.5 and 0.6 gram of the monel, 68.82 and 68.63 per cent nickel were found.

IRON

Dissolve 1 or 1½ gram of sample in 25 c.c. of 1.20 c.c. nitric acid in an 800 c.c. beaker and dilute to 500 c.c. Precipitate the iron with a considerable excess of ammonia and let the solution stand until the iron is well separated. Filter it off; wash the precipitate with 1 : 20 ammonia until the washings are no longer colored blue; then redissolve the iron with 40 c.c. of 1 : 1 HCl; wash the filter free of iron with 1 : 20 HCl and precipitate the filtrate and washings as before with an excess of ammonia; filter off the iron hydroxide; wash it as above; dissolve it as before; dilute the filtrate and washings from this HCl solution to 300 c.c.; heat to boiling; add stannous chloride until the iron is decolorized and 3 or 4 drops in excess; cool; add 35 c.c. of the mercuric chloride solution; stir and titrate at once with a dichromate of potassium made by dissolving 1.225 grams of this salt in water and diluting it to 1 liter. Add the dichromate standard until the solution being titrated no longer gives a blue spot test with potassium ferricyanide when two drops of it are mixed with the same amount of the ferricyanide indicator on the usual porcelain plate. To standardize the dichromate put enough of the iron ore furnished by the Bureau of Standards or of some other equally reliable iron standard through all of the foregoing manipulations as though Ni and Cu were present, and titrate with the dichromate standard. In one such analysis, enough iron ore standard was taken to equal 30 and 60 mgs. of metallic iron in solution. This gave 1 c.c. of the dichromate equals 0.00141 gram of iron.

The mercuric chloride solution is made by dissolving 50 grams of the salt in 1000 c.c. of water.

The stannous chloride is made by dissolving 10 grams of stannous chloride or an equivalent amount of pure tin in 100 c.c. 1 : 1 HCl.

The ferricyanide is prepared by dissolving 0.50 gram of this salt in 100 c.c. of water at the time it is to be used to get the sharpest end-point.

CARBON, MANGANESE, SULPHUR AND PHOSPHORUS

The sulphur is found by the gravimetric method as in plain steels, as given on page 335, the carbon by direct combustion in oxygen, the manganese by the volumetric method given on page 338 and the phosphorus as given on pages 310 to 325.

SOME ANALYSES OF MONEL METAL

	No. 1	No. 2	No. 3
Carbon	0.15	0.10	0.30
Manganese		Trace	3.27
Phosphorus	0.020	0.017	0.045
Sulphur	0.013	0.020	0.063
Silicon	0.236	0.190	0.67
Iron	2.90		3.98
Nickel	68.82	69.18	66.78
Copper	26.95	27.24	24.86

CHAPTER X

PART I

FERRO-MANGANESE

Gravimetric Method.—Dissolve 1 gram of sample in 50 c.c. of 1.20 nitric acid in a No. 4 porcelain dish. Remove the watch glass. Evaporate to dryness. Ignite to low red heat to destroy the carbon. Replace the cover. Dissolve in 40 c.c. conc. hydrochloric acid. Heat until fumes of chlorine have disappeared. Filter into an 800 c.c. beaker. Wash the residue on the filter with 1 : 10 hydrochloric acid until it is free from iron test. Wash it further with water until it is free from chlorine test. Ignite the residue in a weighed crucible and finish for silicon as in steels. The residue remaining, after evaporation of the silicon with HF and a few drops of H_2SO_4, is ignited at a low red; then weighed, the loss of weight being the silica. The weighed residue is dissolved out with a few drops of HCl and added to the main filtrate from the silica as it may contain some manganese, especially if the ferro is high in silicon.

Dilute the filtrate and washings to 300 c.c. Add dilute ammonia until one drop produces a precipitate that fails to dissolve with persistent stirring. Now add 1 drop, only, of 1 : 1 hydrochloric acid. Also pour into the solution 1.5 c.c. of ammonium acetate for every 100 mgs. of metallic iron supposed to be present. (The ammonium acetate solution is prepared by dissolving 50 grams of the salt in 50 c.c. of water. Add dilute ammonia to this solution a drop at a time until it smells very faintly of ammonia.* Add water until the total volume of the acetate solution is 100 c.c.) Heat to boiling. Boil one minute. Permit the precipitate to settle a few moments. Stir in some paper pulp.

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* Or reacts slightly blue with red litmus paper.

Filter hot. Wash fifteen times with hot water containing 2 c.c. of ammonium acetate to 100 c.c. of water.

Redissolve the precipitate with 10 c.c. of hot 1 : 1 hydrochloric acid. Wash the filter free from iron test. Dilute the filtrate and washings to 200 c.c. and precipitate it again as before. Wash the precipitate. Combine this filtrate and washings with the original filtrate and washings. Evaporate all (after adding to the combined filtrates 5 c.c. of 1 : 1 hydrochloric acid) to 200 c.c. Filter if necessary. Add 25 c.c. of ammonium acetate solution. Heat to boiling in a platinum or porcelain dish. Add to the *boiling solution* 75 c.c. of a saturated solution of microcosmic salt, stirring continuously. Add a slight excess of ammonia,* and continue to heat the precipitate and supernatant fluid with frequent stirring until the pink manganese phosphate changes from a flocculent slimy precipitate to a pink crystalline heavy one that settles rapidly to the bottom of the vessel. When cold, filter out the manganese phosphate and wash it with cold water until no milkiness is obtained from the washings on being acidulated with a drop or two of nitric acid and tested with a drop of silver nitrate solution.

Add 10 c.c. more of the precipitant to the filtrate and washings. If a precipitate forms after several hours, collect it; wash it as in the main precipitate. Dry the two filters containing the phosphate. Remove the latter to a large watch glass. Cover it. Burn its filter in a weighed platinum crucible at a low red heat until all black is gone. Now add the small residue, if any, obtained from the filtrate and washings tested with 10 c.c. of the phosphate of sodium and ammonium. When this residue has been burned white at the lowest possible heat, add the main phosphate precipitate and ignite it very slowly to prevent loss by dusting due to liberation of ammonia. Then raise the heat to redness until all carbon is gone. Weigh the precipitate as $Mn_2P_2O_7$. Dissolve the same in 1 : 1 hydrochloric acid, and if the solution contains any insoluble matter such as silicic acid, filter it out. Wash it. Ignite and weigh it. Deduct the weight from the weight of the $Mn_2P_2O_7$, multiply the remainder by 38.69 and divide by the weight taken for analysis to obtain the per cent of manganese.

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* Add only enough of the 1 : 1 ammonia, at first, to produce a slight milkiness. Stir the boiling solution until this milky precipitate becomes heavy and crystalline. Then add the balance of the ammonia, slowly, and with constant stirring to the boiling solution, making sure that an excess of ammonia is used.

If the quick nickel test (see Chapter IX, page 228) shows that considerable nickel or copper is present, these elements should be removed by hydrogen sulphide before making the phosphate precipitations. This can be done as follows: Make the filtrate from the iron hydroxide slightly acid with acetic acid and pass H_2S through it until the sulphides collect and settle out well; filter; wash with H_2S water; concentrate the filtrates and washings until crystallization begins. Dilute with enough cold water to dissolve the crystals; filter again; wash with water, alone, and then proceed with the phosphate precipitation of the filtrate as in the first gravimetric method.

PHOSPHORUS

The precipitate of ferric acetate contains all of the phosphorus. It can be dissolved off the filter and evaporated to moist dryness on the *water bath.* Dissolve the residue in 50 c.c. of conc. nitric acid. Evaporate to about 5 c.c. Rinse into a 5 ounce beaker. Boil with permanganate and finish the phosphorus as in steel.

The phosphorus may be determined on a separate portion by dissolving 1 gram in nitric acid. Evaporate to dryness. Ignite to a dull red. Dissolve in HCl. Convert into nitrate. Filter and finish as in steels.

IRON

Proceed exactly as for manganese up to the point where the small amount of iron and manganese (remaining after the silica has been removed with HF and H_2SO_4), has been ignited and dissolved and added to the main solution. The total main solution will now contain all of the Mn, Fe, Cu, P, and Ni. The iron can be precipitated out with ammonia and redissolved in 1 : 1 HCl and finished for iron by reduction with stannous chloride and titration with a standard solution of potassium dichromate. Or the iron chloride solution can be taken to fumes with 30 c.c. of 1 : 1 H_2SO_4; put through the zinc reductor, and titrated with standard $KMnO_4$. See page 365 and page 443 respectively.

COPPER AND NICKEL

Copper and nickel can be determined by the ferricyanide method as in steel (see pages 205-208).

SULPHUR

Sulphur is obtained as in steels by the gravimetric method.

FERRO-SILICON, SILICON SPIEGEL AND METALLIC SILICON

Silicon and Manganese.—These high silicon materials should be fused with sodium carbonate and potassium nitrate. Fuse * 1 gram with 20 grams of sodium carbonate intimately mixed with 4 grams of finely ground potassium nitrate. Dissolve the melt in water in a platinum dish. Transfer the green fluid and residue to a large casserole. Cover with a watch glass. Add an excess of concentrated hydrochloric acid, keeping the vessel covered. Clean the crucible with a few c.c. of the same acid. Add the cleanings to the acidulated fusion. Heat until all spraying ceases. Wash off the cover, allowing the fluid to flow into the casserole. Evaporate to dryness on a graphite or sand bath. Add 10 c.c. conc. hydrochloric acid. Warm, add 100 c.c. of water and heat for a half hour, or until all salt is dissolved. Filter. Wash the silicious residue free of chloride test. Evaporate filtrate and washings again to dryness. Dissolve, filter and wash as before. Dry the two residues obtained from the first and second filtrations. Roast off the paper from them at the lowest possible heat to prevent loss of silica. Then gradually raise the heat and blast the residues in a weighed platinum crucible until the weight of the ash is constant. Moisten the silica, which should be white, with a few drops of sulphuric acid. Fill the crucible nearly full of hydrofluoric acid. Add the latter cautiously, at first. Evaporate and finish for silicon as in steels. It is safer to evaporate a second time with hydrofluoric and sulphuric acids, using about one-third as much hydrofluoric acid as was used in the first evaporation, to make sure that all silicon has been volatilized.

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* Fuse 0.5 gram in an iron crucible with a mixture of 4 grams of sodium peroxide and 8 grams of sodium carbonate, if silicon, only, is required. Run blanks.

Manganese and Iron.—The filtrate from the second evaporation to dryness should now be divided into two equal portions.*

FIRST PORTION

Phosphorus and Sulphur.—Precipitate with a slight excess of ammonia. Wash the precipitate with water. Dissolve it off the filter with hot concentrated hydrochloric acid, using a little sulphurous acid if necessary. Convert this solution of the iron into nitrate; boil with a little permanganate and finish for phosphorus as in steels, calculating the percentage on a half gram basis.

Sulphur.—The filtrate from the ammonia precipitation is made slightly acid with hydrochloric acid. The sulphur is precipitated with barium chloride and finished as in steels. Deduct a blank obtained on all of the fluxes and acids. If it is desired to use a larger amount of sample for sulphur, it can be determined alone on a 1 gram quantity without dividing into two portions.

SECOND PORTION

Manganese and Iron: Manganese.—This portion is evaporated to fumes with sulphuric acid. The iron is precipitated with ZnO and filtered out. The filtrate is finished for manganese as given for high manganese in soluble ferro-titanium of high manganese content. (Page 59.)

The Iron.—The iron and zinc oxide residues on the filter are dissolved off with hot sulphuric acid and reduced with zinc and titrated for iron in the same manner as given for iron. (See page 365. See also page 443.)

† **The Carbon.**—The carbon can be obtained by combustion of 0.5 gram of the ferro-manganese, etc., with 4 grams of red

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The residue in the crucible after the volatilization of the silica with HF is quite likely to contain a little iron and manganese. It should be dissolved by warming with a little 1 : 1 HCl and added to the filtrate from the second evaporation to dryness before the same is divided into two portions.

† The carbon of ferro-silicon should be determined on a small quantity of the material on account of the great heat generated. Do not burn more than 0.500 gram at a time. Use 4 grams of the red lead.

d; or litharge is equally good as a substitute for the red d.

ESULTS OF A COMPLETE ANALYSIS OF FERRO-MANGANESE "B. H. No. 1"

	Per Cent		Per Cent
rbon	7.15	Nickel	0.096
anganese	80.72	Copper	0.040
osphorus	0.18	Titanium	0.045
lphur	0.028	Iron	10.78
icon	0.45	Tin	0.025
romium	0.015		
nadium	0.041		99.57

CHAPTER X

PART II

RAPID VOLUMETRIC DETERMINATION OF MANGANESE IN FERRO-MANGANESE ORES AND HIGH MANGANESE STEELS, BEING A QUANTITATIVE SEPARATION FROM COPPER AND NICKEL

DISSOLVE 0.500 gram sample in 50 c.c. 1 : 1 HCl, in a No. 5 dish; heat a few minutes; then oxidize solution with 0.5 gram $KClO_3$, using heat; add 50 c.c. 1 : 3 H_2SO_4, and take to heavy fumes. Cool; redissolve in 100 c.c. water together with 10 c.c. 1 : 3 H_2SO_4, heating until all salts are dissolved and only a floating residue of silicic acid and carbon are left. Filter (add a little pulp); wash with dilute sulphuric acid wash until free of iron test. Burn off this residue which should be pure white. If the residue is colored it is weighed; and evaporated with HF and H_2SO_4 acids; ignited and weighed again, getting total silicon in the usual way by loss of weight.

The residue left in the crucible is dissolved in a little HCl, and fumed with a few drops of H_2SO_4, to remove HCl. Dissolve the residue in crucible in water by heating and add the solution to the original first main filtrate which will now contain all of the manganese, copper, and nickel that are in the alloy.

The main filtrate is made nearly neutral with ammonia. The ammonia is added until a faint cloud of iron hydroxide is obtained that will not dissolve on persistent stirring. Add a few drops of H_2SO_4, which should render the solution perfectly clear. Now add 5 grams of ammonium persulphate ($(NH_4)_2S_2O_8$); heat until a dark brown precipitate forms; boil fifteen minutes, and let settle for thirty minutes; pour off clear liquid without disturbing the main precipitate. Wash the precipitate out of beaker onto the filter. Then wash filter and precipitate with cold water twenty-five times.

Transfer filter and all precipitate to original 500 c.c. beaker;

add 50 c.c. 1 : 3 H_2SO_4, to all tests at the same time. Then titrate with standard ferrous ammonium sulphate with constant stirring, until the manganese precipitate is dissolved and the solution is clear. Back titrate the excess of ferrous ammonium sulphate with standard $KMnO_4$ solution. Use the standard solutions as given for titration of chromium and vanadium in steel, 1 c.c. of these solutions should equal about 0.00137 gram of metallic manganese. Results on high ferro-manganese should check as follows:

No. 1. Ferro Mn, 0.5 gram gave 79.26 per cent Mn.
No. 1. Ferro Mn, 0.6 gram gave 79.45 per cent Mn.

Standardize against a ferro-manganese of known manganese value or against a mixture of c. p. $KMnO_4$ and steel drillings put through all operations. c. p. $KMnO_4$ can usually be taken as 99.5 per cent pure, i.e., 34.777 per cent Mn×0.995 equals manganese content of $KMnO_4$. Check the $KMnO_4$ against sodium oxalate before using it or against c.p. oxalic acid.

The following scheme given for oxalic acid can be used equally well for sodium oxalate. The latter salt keeps better than the oxalic acid.

Dissolve 1 gram of the permanganate in 150 c.c. of distilled water, acidulated with 100 c.c. of 1 : 3 sulphuric acid. Warm the solution *slightly*, and add to it 2.0167 grams of the oxalic acid, dissolved in 150 c.c. of distilled water. Warm the solutions a little. if necessary, until the mixture of oxalic and permanganate has become colorless. Titrate the colorless solution with a dilute permanganate standard of known oxalic value. The one used in the analysis of crucibles and plumbago answers very well. 1 c.c. of this standard equals 0.00144 gram of oxalic acid (see Analysis of Graphite, XVI, page 397). Suppose 25.5 c.c. of this standard are required to render the decolorized mixture a slight pink that will remain permanent for thirty seconds, therefore 25.5×0.00144 or 0.0367 equals the excess of oxalic acid in the mixture. Hence $2.0167-0.0367=1.98$, or the amount of oxalic acid oxidized by the 1 gram of the permanganate. By the equation

$$2KMnO_4+5H_2C_2O_4+3H_2SO_4$$
$$=K_2SO_4+2MnSO_4+8H_4O+10CO_2.$$

we have 316.3 grams of $KMnO_4 = 630$ grams of $H_2C_2O_4 + 2H_2O$, or oxalic multiplied by 0.502 equals permanganate; $1.98 \times 0.502 = 0.99396$, or the 1 gram of permanganate contains 0.9939 gram of 100 per cent $KMnO_4$. The precaution must be taken to use sulphuric acid that does not bleach permanganate on warming a few drops of the dilute permanganate standard with 150 c.c. of the acid.

The foregoing scheme is the author's adaptation of G. v. Knorré's persulphate method for manganese in iron, steels and ores. It is a quantitative separation of Ni.*

Von Knorré credits H. Marshall † with precipitating manganous sulphate solutions with $K_2S_2O_8$ as MnO_2 and that H. Marshall in his later paper, "Detection and Determination of Quite Small Amounts of Manganese," ‡ finds that on warming manganous solution with silver nitrate that permanganic acid is formed; and in the same paper by heating manganous sulphate solutions with persulphate, under the conditions as given, that manganese is separated out, quantitatively.

Von Knorré states that under these conditions cobalt is precipitated also with the manganese, and interferes, and must, therefore, be removed by H_2S or some other method. That he did not succeed in getting a quantitative separation of either nickel, copper, or zinc, but that these three elements do not interfere with the quantitative determination of the manganese.

The precipitation of the manganese takes place as follows:

$$MnSO_4 + (NH_4)_2S_2O_8 + 3H_2O = MnO_2 \cdot H_2O + (NH_4)_2SO_4 + 2H_2SO_4.$$

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* Z angew Chem , 14, 1149 (1901)

† J Chem. Soc , 1891, 59, S. 771-786.

‡ Chem. News, Bd. 83, 1901, S. 76.

CHAPTER X

PART III

DETERMINATION OF BORON IN IRON

THE method of Wherry * was applied to the determination of small percentages of boron in iron by J. M. Lindgren.† He states that he found the principles as set forth by Wherry to be entirely feasible. Lindgren proceeded in the following way: "Three grams of iron are dissolved in a round-bottom flask of 800 c.c. in a mixture of 10 c.c. each of 1.4 sp. gr. nitric acid and 1.2 sp. gr. HCl. When solution is complete, cool, and precipitate the iron with dry c. p. calcium carbonate to a pasty mass. At this stage the volume should not be much over 30 c.c. Now add, all at once, twice as much more calcium carbonate and stir vigorously.

"The pasty mass of precipitated iron, etc., is now diluted with about 300 c.c. of water. This water must be carbon-dioxide free. Attach a reflux condenser to the flask, start the water through the condenser, and then bring the contents of the flask to the boil and continue boiling until the CO_2 is removed. At least thirty minutes' boiling is recommended as sufficient to remove CO_2."

The next operation is to filter out the iron hydroxide. Lindgren recommends that acid-washed asbestos be mixed in with the hydroxide of iron to aid in the filtration and washing of the hydroxide. Add the fiber in a wet condition, and use 50 c.c. of the boiling hot wet fiber. Boil the mixture of hot wet fiber (which is boiled a while in water before it is mixed in the iron precipitate) and hydroxide of iron for several minutes. Filter by suction. Lindgren recommends the use of a 15 cm. diameter

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* Jour. Am. Chem Soc, 30, 1687 (1908).

† Ibid., 37, 1137 (1915).

Büchner funnel and a splash trap. Wash the precipitate ten times with boiling water.

The filtrate and washings in the flask are cooled and titrated with N/10 KOH (free of carbonate). After a few drops of phenolphthalein are added, add the alkali standard until a pink color appears. Now add 1 gram of mannite and continue to add KOH until a second pink is obtained. To make sure that the reaction is complete, Wherry recommends to add more mannite. If this causes the pink color to disappear, the reaction is incomplete. Then add more of the KOH standard, a few drops at a time until a pink color is again obtained. Again add 1 gram of mannite and if the pink color does not again disappear, the reaction is complete.

Blanks must be run, using steel or iron free of boron, adding to the same known amounts of a standard solution of fused boric acid. 3.5 grams of the fused boric acid dissolved in 1 liter of water, free of CO_2. The boric acid is fused in a platinum dish. Do not use porcelain. Lindgren gives the relation between 1/10 N KOH and the boric acid solution as 8.75 c.c. KOH requires 8.68 c.c. of the B_2O_3 solution.

Lindgren states that if the precipitation of the iron with calcium is properly carried out, as described, no boric acid will remain with the iron hydroxide. He gives the following recoveries:

Per cent boron taken	0.038	0.188	0.424	0.850
Per cent boron found .	0.044	0.194	0.388	0.840

Having read Wherry's original article on "The Determination of Boric Acid in Insoluble Silicates," the author believes it advisable to give the following points from it: If the mineral is fused with an alkali carbonate and extracted with water, boric acid will remain in the water-insoluble residue. If, on the other hand, the fusion is dissolved in acid, and the iron, etc., are precipitated with ammonium, boron will be carried out with the hydroxides, to which it persistently clings even after several reprecipitations. Hence the use of calcium carbonate to separate the hydroxides.

Wherry fuses the mineral with 3 grams of sodium carbonate for fifteen minutes. Dissolves in 20 to 30 c.c. of dilute HCl; adds a few drops nitric acid to oxidize any ferrous iron; places the whole solution in a 250 c.c. round-bottom flask; heats nearly to boiling; and adds dry precipitated calcium carbonate and connects the condenser and boils for ten minutes. He filters out the precipitate, washes it with hot water, keeping the volume below 100 c.c. He returns the filtrate and washings to the boiling flask; adds a pinch of calcium carbonate; connects the condenser and boils again. If the precipitate has a red color, filter it out; wash; add 4 to 5 drops of phenolphthalein solution, and titrate the filtrate slowly with the alkali standard to a pink. (Wherry uses 1/10 N NaOH) as already described, adding 1 gram mannite, etc., until a permanent pink is obtained.

Boric acid should never be boiled openly, as it is very volatile in steam, hence the use of the condenser. For a return condenser a simple straight tube about 2 cm. wide by 75 cm. long is recommended placed vertically through the stopper of the boiling flask.

The bulk of the solution should be small for the titration, as the end-point is not very sharp if the liquid is too dilute. Finally, just before titration all free CO_2 must be removed. This is done by attaching the suction to the filtering flask, first removing the Buchner filtering funnel. The filtering flask is closed with a solid stopper, and the suction again applied. This should produce a further boiling without any more heating and the free CO_2 is sucked away. All CO_2 and bicarbonates must have been removed or the titration will give a low value. Continue the suction until all fine bubbles cease to form due to the reduced pressure. Suction must be applied cautiously or the hot liquid may boil over.

To insure the complete decomposition of any calcium bicarbonate, and to make certain that all sesquioxides are completely precipitated, the solution to which the dry calcium carbonate was added must be boiled for at least ten minutes. Indeed, in minerals containing much iron, some of the latter may still remain in solution. A little calcium carbonate should be added to the first filtrate and washings from the main iron; boil; filter; and wash again.

To hasten filtration when the precipitate is large, Wherry used an 8 cm. Büchner funnel, covered first with a layer of asbestos and then by a large filter paper folded around a bottle of a slightly less diameter than the funnel. A single stirring with hot water is said to be enough. The filtrate and washings must be small as the end-point is not sharp in too dilute a solution.

After the prolonged boiling (with condenser) to decompose all bicarbonate and precipitate the sesquioxides, the free CO_2 is removed by suction. The mouth of the flask is plugged with a solid stopper and the suction is applied. Use a splash trap to prevent loss of fluid by spraying or boiling up when the pressure is reduced. When the temperature has fallen to about 50°, the suction is stopped by disconnecting the pump.

The sodium hydroxide (or KOH) used in the titration can be freed of CO_2 by the method of Winkler. The carbonate is precipitated by adding barium chloride to a measured amount of the NaOH. Now titrate the NaOH with a standard acid, using phenolphthalein as an indicator.

In titrating the boric acid by the present method, the excess of calcium chloride in the solution will immediately precipitate all of the carbonate from the alkali standard, producing a slight turbidity. The first drop of alkali added to the solution containing the boric acid should produce at once a distinct pink which will disappear on stirring. If no pink is obtained, it shows that calcium bicarbonate is still present, having escaped decomposition, in the boiling. In this case acidify the solution; add a slight excess of calcium carbonate and boil again.

The use of mannite is much to be preferred to glycerole. Jones is credited with first using mannite. Mannite is said to give a sharper end-point and much less of it is needed. The c.c. of alkali used, multiplied by 0.0035, gives directly the amount of boric acid (B_2O_3) present.

Wherry states that, in some cases, it is necessary to redissolve the iron and reprecipitate it with the calcium carbonate to insure the complete separation of the boric acid from the hydroxides formed, performing these operations three or four times. Filter and wash each time and determine the boric acid in each set of filtrates and washings, summing all together to get the total. Lindgren claims this is not necessary. Most likely Wherry is right when large quantities of iron, aluminum, and boron are present.

$$2B_2O_3 + Na_2CO_3 = Na_2B_4O_7 + CO_2.$$

CHAPTER XI

PART I

THE DETERMINATION OF CARBON IN IRON AND STEEL BY DIRECT IGNITION WITH RED LEAD OR LITHARGE *

THE author's experience with this method for the determination of carbon, together with some notes, may prove of interest.

The solution of steel drillings containing large percentages of chromium, tungsten or molybdenum in double chloride of copper and potassium causes more or less loss of carbon as hydrocarbon. Especially sensitive to such loss are the carbides that are separated by the double chloride from steels in which are 10 or 12 per cent of molybdenum together with several per cent of chromium.

These carbides may lose some of the carbon by contact with dilute acid, or with the oxygen of the air during washing with *suction*, or during the subsequent drying of the carbide at the temperature of boiling water.

In the spring of 1900 the writer made an analysis for carbon of a steel containing 3.8 per cent of chromium, applying the ordinary method † of dissolving the borings in acid double chloride of copper and potassium, filtering on an asbestos plug, washing the carbide residue alternately with distilled water and a mixture of one part of hydrochloric acid and twenty parts of water. The residue was then washed with water, alone, to remove the acid. After drying the washed carbide in a water oven, it was burned with purified oxygen in a red hot porcelain tube containing about 13 cm. of copper oxide. The products of the combustion were passed through granulated zinc of 20-mesh fineness, then through anhydrous calcium chloride, and then through phosphoric anhydride. The purified carbon dioxide was absorbed and weighed in potash bulbs. Duplicate analyses by this method failed to check.

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* A preliminary paper was read at the December, 1905, meeting of the Pittsburgh Section of the American Chemical Society.

† See pages 297 to 301.

A series of analyses of these borings were made. The acid wash *when used* was alternated with distilled water, and the washing was then completed with distilled water, alone, to remove acid.

	Kind of Wash	Washings, Number	Carbon Found, Per Cent
1	20 parts H_2O to 1 part HCl	20	1.65
2	100 parts H_2O to 1 part HCl	20	1.52
3	100 parts H_2O to 1 part HCl.	2	1.909
4	100 parts H_2O to 1 part HCl .	2	1.943

In August, 1902, the process used in the foregoing, (3) and (4), was applied to a steel containing 4 per cent of chromium and 4 per cent of molybdenum with the following absence of agreement:

First analysis gave 1.28 per cent carbon.
Second analysis gave 1.53 per cent carbon.
Third analysis gave 1.33 per cent carbon.
Fourth analysis gave 1.29 per cent carbon.

The thought occurred that perhaps the carbide obtained from molybdenum steel gives up part of its carbon as hydrocarbon on being brought into contact with the air during stirring. No heat was applied to hasten the solution at any time. A number of trial analyses were made in which the time of stirring was varied and also the acidity of the copper and potassium chloride solution. In the following, 2 grams of the drillings were dissolved in 180 c.c. of the double chloride solutions. By *acid* solution is meant a solution prepared by dissolving 600 grams of double chloride of copper and potassium in 1500 c.c. of distilled water acidulated with 175 c.c. of concentrated hydrochloric acid. By *nearly neutral* solution is meant the same as the acid solution except that but 25 c.c. of concentrated hydrochloric acid were added to the 1500 c.c. of distilled water.

The *neutral* solution consisted of 600 grams of the double chloride, 1500 c.c. of distilled water, and *no* acid. The results obtained are given in the following table:

STEEL CONTAINING 4 PER CENT MOLYBDENUM AND 4 PER CENT CHROMIUM

Kind of Steels	Kind of Solvent	Time of Stirring, Minutes	Time in the Solvent with No Stirring, Hours	Percentage of Carbon Found
No. 1 steel	acid	20		1.53
No. 1 steel	"	20		1.48
No. 1 steel	"	10		1.64
No. 1 steel	"		12	1.49
No. 1 steel	"		24	1.52
No. 1 steel	nearly neutral	8		1.60
No. 1 steel	"	8		1.55
No. 1 steel	acid	3		1.60
No. 1 steel	neutral	6		1.593
No. 1 steel	"	6		1.606
No. 2 steel	neutral	4		1.679
No. 2 steel	"	6		1.734
No. 2 steel	acid	4		1.758
No. 2 steel	"	4		1.66

A combustion of the 4 per cent chromium, 4 per cent molybdenum steel (No. 2), by the red lead process described below yielded 1.734 per cent carbon.

An examination of the foregoing table shows that both in the No. 2 and the No. 1 steels the highest result was obtained when the acid solvent was used, and also the lowest results.

Short stirring gave better agreements than the longer periods of stirring, but had evidently not eliminated all of the causes of loss. Perhaps there is loss of carbon when the carbide is being dried in the water oven. Further, it is practically impossible to regulate the suction so as to expose the residues, during washing, to exactly the same amount of air in each analysis.

Two grams of the No. 2 steel were stirred twenty minutes with 180 c.c. of the acid solution, then transferred to the asbestos plug. Air was next drawn through the residue for fifty minutes; the amount of carbon obtained was 1.347 per cent. Two determinations of the same steel were made with sixty minutes' stirring but with the least possible exposure to air by suction; 1.63 per cent and 1.68 per cent carbon were found. In view of these results the practice was adopted of always keeping a layer of distilled water over the carbide during the washing. As soon as one layer, or covering of water, was drawn off, another was immediately supplied.

This treatment was applied to a group of ingots containing 11 per cent molybdenum and some chromium. The neutral solution gave the higher results, as shown by the following table:

Acid Solvent Per Cent Carbon	Neutral Carbon Per Cent Carbon
0 52	0 60
0 46	0 56
0 53	0 59

The same process of short stirring and least possible exposure of the carbide residue to air by suction, together with the use of a neutral solvent, was adopted for a series of ingots containing 12 per cent molybdenum and several per cent of chromium. It failed almost completely. For convenient comparison the results obtained in these latter experiments are shown in a column parallel to those obtained, at a later date, from the same samples by the red lead combustion method. (Page 261.)

One well-known laboratory obtained 0.72 per cent carbon, and another, equally experienced, reported 0.64 per cent carbon on the S. H. S. sample.

This untrustworthiness of the double chloride process for separating carbon in steel of high molybdenum and chromium content led to a search for some method of obtaining the percentage of carbon by burning the entire substance. Having about this time noted Brearley and Ibbotson's statement that steel drillings that will pass a 20-mesh sieve and have been mixed with about three times their weight of red lead can be decarbonized in a red hot porcelain tube, it was decided to attack the molybdenum steel in this manner. The results obtained from the molybdenum steels are given in the table below and need no comment:

Sample 12 Per Cent Mo Steel Containing Cr	Results Obtained by the Neutral Solution Per Cent Carbon	Results obtained by the Red Lead Process Per Cent Carbon
No. 1	0.54 0.72	0.80 0.79
No. 2	0.81 0.51	0.76
No. 3	0.66 0.49 0.51	0.82
No. 4	0.54 0.58	0.81
"2d trial"	0.47 0.61	0.88 0.85
No. 5	0.61 0.88	0.88 0.87
No. 6	0.49	0.73
S. H. S.	0.69 88 0.66 0.68 75	
No. 7	0.66 0.52	0.94 0.939
No. 10	0.76 0.75 0.62	1.00
No. 11	0.72 0.52	0.80

The method was first applied to plain carbon steels, pig iron, and white iron, and was found to be perfectly accurate.

After more than eighteen months' daily use of the red lead for the determination of carbon in steel, pig iron, alloy steels, and ferro alloys, i. e., in 1905, the details that have been found useful and reliable are as follows:

If part of the borings are coarse, the thin curly portions or 30- to 60-mesh sievings are selected. Two grams of such drillings and 2 grams of the red lead are weighed into a glass-stoppered 60 c.c. weighing bottle. The bottle is then shaken to mix the drillings and lead oxide.

The steel sample submitted for analysis is drilled with a flat or diamond-pointed drill. This style of drill will grind many of the drillings to 20-mesh fineness in the case of soft or annealed steels. If the steel be unannealed and of a carbon content ranging from about 0.35 per cent carbon and higher, thin curly drillings are obtained which decarbonize readily by reason of thinness. If the drillings do not exceed 20-mesh, as in siftings, 4 grams of red lead will completely decarbonize 4 grams of the steel. Care is taken at all times to cover bulky drillings with the oxide of lead, as any drillings that project above the main body of the charge are likely to escape oxidation.

For soft steels and annealed steels two sieves are used. One has a 20-mesh gauze and the other one a 60-mesh gauze. Those drillings that pass the 20-mesh gauze but do not pass the 60-mesh sieve are used for analysis.

This arrangement rejects the fine dust and the thick drillings. When very small pieces of steel are received they are drilled with $\frac{3}{16}$ inch diameter twist or straight drills. All sizes of the flat, or diamond point, drills are kept at hand from $\frac{1}{4}$ inch diameter to $\frac{7}{8}$ inch. Any good mill blacksmith can make the flat drills. By these means it is rarely, if ever, necessary to resort to the copper and potassium chloride separation of the carbon. In the laboratory of the Park Steel Co., where many combustions are made each day, covering a range from 0.04 to 3.5 percent carbon, the writer does not recall more than a single instance in a year's time when it was necessary to resort to the double chloride process.

The mixture of lead oxide and drillings is transferred from the weighing bottle to clay boats.* The size, 15×75 mm., is mostly used, being convenient. The boats are slipped into † clay tubes ‡ of $\frac{3}{4}$ inch inside diameter × 24 inches long. Two furnaces with their tubes are operated at the same time. Formerly, the outlet ends of these tubes were filled for a distance of 125 mm. with granulated copper oxide. Later the copper oxide was found to be unnecessary. Oxygen is used during the combustion. It passes through a jar containing pieces of caustic potash (Fig. 4). It next bubbles through a solution of

The author now uses the clay boats for all combustions, and clay tubes.

† Three-quarter inch inside diameter fused silica tubes are very desirable for this work. The litharge fumes and spills, however, will, in time, destroy them. The author sometimes uses a small inner cylinder of platinum just large enough to hold the boat. Iron oxide will flux silica tubes. (See clay tubes, page 294.)

‡The author is now using tapered clay combustion tubes. (See page 294.)

potassium hydroxide contained in a safety apparatus (Fig. 5), and is then dried in jars of soda-lime and calcium chloride of the design given in Fig. 4. This drying and purifying apparatus can be readily arranged and securely fastened in a space 250 × 406 mm.

The combustions are operated in the usual manner. The tube is heated to a yellow heat (980° C.). The combustion tubes are constantly kept hot so that the combustion commences almost as soon as the stoppers are inserted. While the boats are being charged the oxygen is passing slowly through the tubes and the weighing and absorbing apparatus which has been previously weighed and attached. (This weighing apparatus is shown in Fig. 6. It was designed by the writer as a substitute for the different forms of potash bulbs now in the market. It is made of heavy glass. It is easily kept clean, is not top-heavy, and does not occupy much space in a balance case.) As soon as the steel begins to burn, there is, at first, a rapid evolution of gas which quickly ceases. More oxygen is then turned into the apparatus from the steel cylinder so that a slow bubbling is maintained through the weighing apparatus. When the oxidation of the charge is completed, the oxygen begins to rush through the apparatus at a high rate of speed. The flow of the gas is quickly checked to a normal rate, that is, it is checked so that it passes through a safety apparatus (Fig. 5) at a rate of about twenty-six bubbles per ten seconds. The stream is evenly distributed to

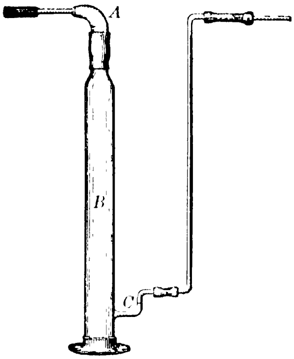

Fig. 4.

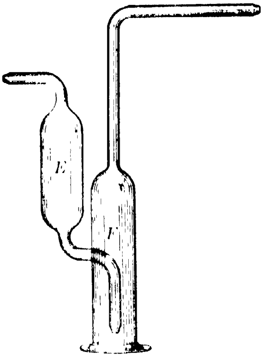

Fig. 5.

the two combustion tubes by means of a Y-tube and screw pinch-cocks. The stream passes through the weighing apparatus (Fig. 6) at the rate of 250 c.c. every ten minutes, which is the normal speed. When the combustions are completed in both sets of apparatus, as indicated by the passage of the gas at a high rate of speed, the normal is then maintained through the hot tubes ten minutes longer to insure complete oxidation and that

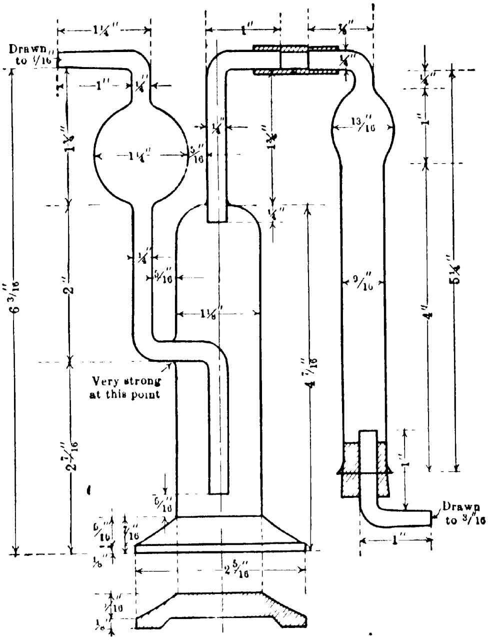

Fig. 6.

all of the carbon dioxide has been carried to the weighing apparatus. The products of the combustion pass through a purifying train shown in Fig. 7. The train connects with the glass tube leading from the outlet end of the combustion tube, by means of heavy combustion rubber tubing, at *H*. The gases pass through the cylinder *I* which contains a column of granulated zinc of 20-mesh fineness. The use of granulated zinc to remove acid and chlorine in carbon combustions was first suggested by Dr. Edward S. Johnson. Cylinder *I* is 254×13 mm. The zinc is held in place with plugs of glass wool. The gases next enter a cylinder *J* which contains a column of phosphoric anhydride. The phosphoric anhydride powder is held in place with plugs of ignited asbestos. Cylinder *J* is 178×13 mm. Glass wool plugs should not be used in *J*, as they become clogged after a few combustions. Ignited asbestos is free from this objection.

The carbon dioxide, which is now freed from litharge and sulphur, and any acid fumes by zinc, and from any moisture by the phosphoric anhydride, enters the weighing apparatus *L*. The weighing apparatus is charged with 20 c.c. of potassium hydroxide consisting of one part of caustic potash dissolved in 1 part of water. The drying tube *C*, Fig. 7, is filled with small pieces of *dry* caustic potash obtained by quickly cracking dry sticks of caustic potash in a porcelain mortar. Each end of the drying tube *C* contains a plug of asbestos or glass wool. Before inserting the rubber stopper in *C*, care must be taken to free the surface of the tube *C* from any moist caustic potash, as potassium hydroxide causes decomposition of rubber, resulting in continuous loss of weight.

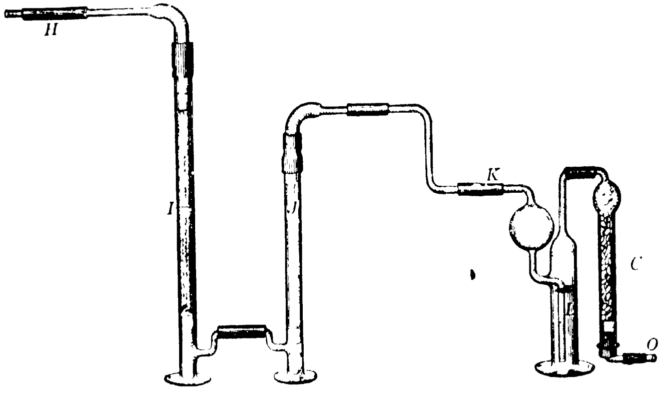

FIG. 7.

During the passage of the oxygen the outlet *O*, Fig. 7, is protected from the ingress of moisture or impure air by a guard tube filled with small pieces of caustic potash. This guard tube is not shown in Fig. 7. All parts of the apparatus shown in Fig. 7 are connected by heavy wall pure rubber tubing.

When the combustions are completed the weighing apparatus is detached from its train, and the outlet of the train is closed with a glass plug.

It is accurate to weigh the absorption apparatus (Fig. 6) filled with oxygen and thus avoid aspirations. In this way combustions can be carried through in twenty minutes.

* The red lead used in this work must be thoroughly mixed and ground free of lumps before its carbon content is determined. The so-called pure red lead costing about nine cents per pound in 50-pound lots is found satisfactory for the purpose. Blank combustions with 4 grams of red lead are at present yielding 6 mgs. of carbon dioxide which are deducted from each determination. Blank combustions or analyses of standard steels should be made each day. The red lead is kept in tightly stoppered bottles.

Zirconia composition tubes, tapered tubes, have been in use for several years in the author's laboratory; boats of zirconia also.

The apparatus shown in Fig. 5 was designed as a safety apparatus to prevent the potassium hydroxide solution from blowing over into the rubber tubing from any cause. The oxygen enters the chamber *E* and bubbles through chamber *F*, which is filled to one-third its capacity with potassium hydroxide solution consisting of 1 part of caustic potash dissolved in 1 part of water. *F* is 35 mm. outside diameter by 170 mm. long. Fig. 4 shows a tower or jar that is used as a container for small pieces of stick caustic potash for purifying the oxygen. The pieces of apparatus shown in Figs. 4, 5 and 7 were designed by the writer to avoid the use of rubber stoppers.

† The following results attest the accuracy of the red lead process:

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* On one occasion a lot of red lead was purchased that was not uniform. No amount of mixing improved it. It was rejected. Subsequent kegs gave no trouble. Good commercial red lead gives about 0.004 gram of CO_2 per 4 grams and is very uniform.

† Reprinted from The Journal of the American Chemical Society (with additions), Vol. XXVIII, No. 7, July, 1906.

Name of Sample	Weight of Sample Taken, Grams	Weight of Lead Oxide Used, Grams	Per Cent Carbon by Red Lead	Per Cent Carbon by Double Chloride
S. S. Co. carbon steel	3	9	0.0395	0.115
No. 690			0.985	0.96
No. 350, tungsten steel			1.285	1.29
No. 353, tungsten steel			1.338	1.351
No. 22, high per cent nickel steel			0.698	0.696
No. 14, nickel steel			0.147	0.150
S. XIX, high per cent tungsten steel			2.10 2.39	2.35
Washe metal	1½	1½	3.56 3.65	3.59
Washe metal	1½	3	3.58	
C. B. pig metal	1½	¾	4.01	
C. B. pig metal	1½	1½	4.01	4.04
Soft O. H. steel No. 1	6	3	0.192	0.185
Soft O. H. steel No. 2	8	1	0.097	0.077
Soft O. H. steel No. 3061	6	3	0.156	0.115

CARBON IN FERRO-CHROMIUM

In applying the red-lead process to ferro-chromium, it was found that the maximum carbon in the 65 per cent chromium

Ferro-Chrome	Weight of Sample Taken, Grams	Weight of Red Lead Used, Grams	Per Cent Carbon Found
Sample A	1	2	7.26
"	1	3	7.54
"	1	4	7.72
"	½	3	7.73
Sample B	½	2½	7.03
"	½	4	7.00
Sample C	½	2½	6.46
"	½	3½	6.55
Sample D	1	1	6.05
"	1½	¾	5.17
"	1	2	6.403
"	1	4	7.094
"	1	3	7.15
Sample E	1	4	7.07
"	½	4	7.18

alloy was obtained by burning the alloy with three to four times its weight of red lead. (See table at bottom of page 267.)

A red hot body of copper oxide hastens breakage of combustion tubes by causing unequal cooling strains when the furnace flames are lowered or extinguished for any reason.

In February, 1906, the copper oxide was first omitted from one combustion tube. The space ordinarily occupied with copper oxide was filled, loosely, with ignited asbestos. The following results indicate that the use of copper oxide in combustion with red lead is unnecessary:

Sample	With Copper Oxide Per Cent Carbon	Without Copper Oxide Per Cent Carbon
3 square steel	1.479	1.477
No. 288	1.175	1.175
6 S	0.207	0.207
No. 1193	0.712	0.692
No. 7013	0.520	0.538
C. No. 2	1.18	1.51
No 2703	0.316	0.309
No. 385	0.425	0.439
No. 7014	0.396	0.393
No. 7013	0.401	0.397
No. 1241	0.75	0.765
C. No. 3	1.281	1.283
No. 7015	0.409	0.407
No. 7016	0.481	0.478
No. 7017	0.312	0.315
No. 7018	0.425	0.43
No. 7020	0.431	0.431
No. 1200	0.73	0.75
Ferro-manganese	6.31	6.39
Mixture of plumbago and clay	45.96	46.04
Pig iron "B"	3.61	3.58

Sampling.—Two grams of red lead to the same weight of steel are sufficient where siftings of from 20- to 60-mesh, or thin curly drillings that can be packed in a close mass are obtainable. It is extremely rare that such a sample cannot be gotten; if the chemist will only insist that a piece of the steel be sent to him instead of drillings that frequently are coated with a film of grease,* or contain bits of paper, fine fibers of wool waste, leaf tobacco, blue steel, rust, scale, or clay, he can then take his own drillings with the proper absence of variety.† Most chemists are aware that the center of the cross-section of a square bar or round piece of steel often contains as much as 50 per cent more phosphorus, sulphur, and carbon than the outside part. Further, that sheet steel just as often varies as much in these elements, and *in spots*. Hence, to get an average and fair sample, a square bar or a round one should be drilled from the surface toward the inside, either halfway or all of the way through the sample when practicable.

If for any reason the steel must be drilled on end then a row of holes of *equal* depth should be drilled all of the way across the section and all of the drilling mixed together. In like manner a flat bar or sheet should have a series of holes of the same depth drilled across it from edge to edge. A failure to observe these precautions often results in disputes between buyer and seller.

It is surprising from what small and hopeless looking pieces of steel one can extract enough drillings of the proper cross-section for direct combustion analysis with a good assortment of small drills and a little experience.

The Taking of Drillings or Millings Suitable for Analysis.— In this connection one should read the remarks at the close of Chapter XI, Part I (page 271). Fig. 8 shows a drill press operated with a direct connected constant speed motor of 3½ h. p. The press is equipped with an adjustable vise which can be turned at any angle so that small and very irregular pieces of steel can be gripped and held immovable during the drilling.

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* Clean greasy or oily drillings by repeated extractions with ether. Place the drillings in a small weighing bottle and shake them up with enough ether to cover them. The ether will become yellow if the drillings are greasy. Pour this ether off. Pour on some clean ether and repeat the extraction; pour off, and so on, until the ether is no longer colored. This process removes lint at the same time, as one can readily notice. The fluid will be seen to be full of many short fibers, at times.

† Another cause of variable results is surface decarbonization, or bark. When steel shows bark all drillings should be rejected until the drill passes through the decarbonized zone. If the sample is too thin for this precaution, then the condition of the steel should be noted on the chemist's report. See pages 423 to 429 on the cause of bark.

FIG. 8.

The drill chuck is large enough so that the set screw that holds the drill in place does not protrude, thereby preventing any possibility of the operator getting his sleeve caught and his arm twisted around the spindle. To prevent particles of oil or grease from getting in the drillings, thereby ruining the same for the determination of carbon by combustion, the author had a large disk of sheet iron put on top of the chuck as shown. This precaution proved invaluable.

Fig. 9 gives the author's device for sampling material that cannot be drilled by reason of extreme thinness of cross-section.

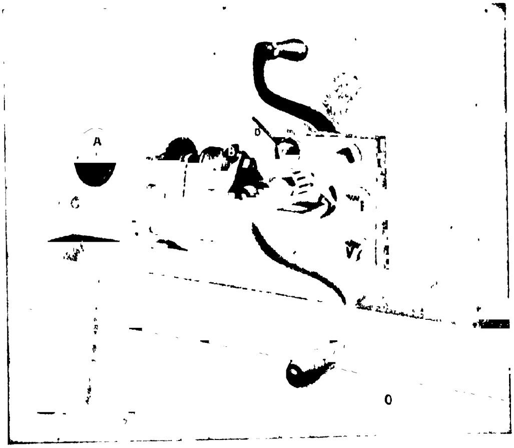

FIG. 9 *

At this writing quite a number of copies of this tool are in use both at home and abroad.

LABORATORY MILLING MACHINE FOR SAMPLING STEEL †

In certain kinds of steel the author encountered much difficulty in getting samples of sufficiently small mesh for the determination of carbon by the direct method described by him several years ago.

The trouble was confined to thin sheets, wire, hack-saw steel,

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* On page 274 this milling machine is shown with a power attachment, which is preferable when many samples are to be milled.

† Reprinted from Journal of Industrial and Engineering Chemistry

band-saw steel, razor blades, resistance ribbon, nails, and small samples of all kinds that are irregular in shape and difficult to hold in the drill press vise.

The machine shown in the illustration afforded a successful means of avoiding various time-consuming expedients.

The sample *D* of wire, for example, is held in the vise *V-V*. The millings are taken by means of a cutter, made of the best high-speed steel, and are caught on a piece of cardboard at *C*.

The automatic feeding device at *A* is hastened in its action by tightening the screw at *B*.

If millings are taken from very small gauge wire, a large sample can be obtained more quickly by twisting the strands together after cleaning the same with emery cloth, if rusty. In this way the cutter mills as many lengths as desired at one time. This machine mills copper wire with great ease. It makes easy the getting of the large quantity of material required for the determination of oxygen in copper, for example. In like manner, when it is desired to expedite the taking of large samples from extra thin sheets of metal, these sheets can be cut in strips with tinner's shears. The strips from the same sheet can then be laid one on the other, clamped in the vise, in layers, and all milled at once.

The milling cutter can be sharpened several times.

It is desirable, and well worth the small amount of time involved, to anneal all samples received, if they are not already in a softened state. This operation can be done in a half hour's time by heating the sample to 800° C. (bright red), quenching at once in water and then holding at 620° to 630° C., for twenty minutes (low red). Samples that cannot be quenched for any reason should be annealed as described under Annealing, pages 414 to 421.

The millings obtained by this laboratory tool are not sifted, as they are just right for direct determination of carbon by combustion in oxygen.

If the sample submitted is sufficiently rigid, it does not need to be held by both ends, as in the case of the sample of wire.

This machine, as illustrated, has been in use in the writer's laboratory for some years. Since its introduction, the samplers no longer dread the appearance of wire and steel ribbon, this work being now a mere matter of easy routine.

The first cost was a bagatelle compared to the saving of labor in one month.

The Taking of Drillings or Millings.—*Hard and Soft Layers.* —Samples of steel are frequently submitted that consist of welded layers of hard and soft steel, such as soft-center, three-ply knife, inserted and overcoat axe bit, jail-bar, safe steel, and "faced" hoe. Quite often, when there are but two layers, the hard one can be stripped from the soft one by placing the composite in a vise and driving a cold chisel between the layers. The hard strip can be annealed and milled. If stripping is not feasible, then the sample should be annealed and the hard portion drilled with a shallow, diamond pointed, wide drill of 1⅜ inches diameter at the wings.

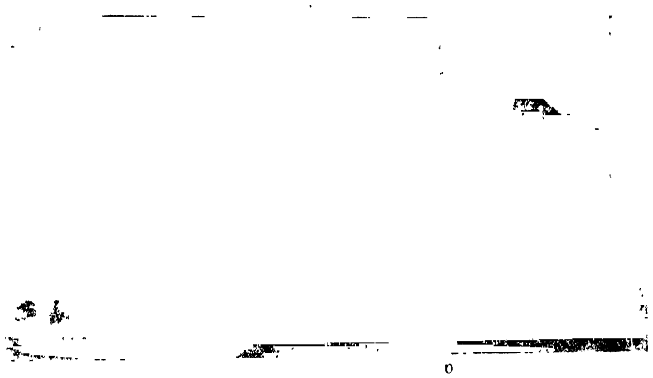

Photo A

If it is desired to drill a hard layer between two soft ones, the whole piece can be heated to bright redness and quenched in water. The soft layers can then be machined, or ground off. The hard center can then be annealed and milled.

It is a little more difficult to obtain drillings or millings from a soft layer lying between two hard ones. In such a case the cross-section of the steel should be polished fairly smooth and etched with 1.20 nitric acid to clearly define the exact depth of the layers. The higher carbon zones will be plainly marked as black bands while the soft steel will retain its natural color. The sample is annealed before the etching is done. so that one of the black layers can be machined away. The white layer can then be drilled with a wide, flat drill, after quenching from 1500° F.

In general, it is a good thing to etch the polished section of samples, as often, by so doing, hard layers or insertions are discovered when least suspected; or curious defects, or spots or streaks, or segregations are revealed.

Test for Segregation, Closed-up Pipe and Flaws.—Segregated steel becomes deeply pitted, in the segregated parts, on being suspended in sufficient 2 : 10 sulphuric acid to maintain a continuous evolution of hydrogen for several hours. Polish the piece fairly bright and smooth before making the test. Etch cold. Photo A shows hidden flaws revealed by deep etching.

CHAPTER XI

PART II

THE DETERMINATION OF CARBON IN STEEL, FERRO-ALLOYS, AND PLUMBAGO BY MEANS OF AN ELECTRIC COMBUSTION FURNACE *

IN 1908 it occurred to the author that a special resistance wire could be applied to the heating of combustion tubes. A drawing was prepared for a furnace of a muffle type to heat four tubes lying in the same plane and parallel.

After some correspondence it was agreed at first to try a single tube furnace. It consists of a steel tube 295 mm. × 76.3 mm. containing a non-conducting packing of solid infusorial earth. In the center was a quartz tube wound with the patent wire. Inside of this tube was placed another of the same material of 19 mm. I. D. × 600 mm. long in which the combustions were made.

Photo No. 7, page 276, shows the author's present combustion apparatus giving the arrangement of two furnaces in parallel The front furnace train at the exit end of the combustion tube is shown. The same portion of the train is not shown for the rear furnace. *R*, *R* show the author's design in rheostats.

A. Mercury pressure gauge for detection of leaks and stoppages.
B. Safety jar for potassium hydroxide solution, preventing solution from backing over into rubber tubing.
C. Jar for stick potassium hydroxide or for any solid drier or absorbent.
D. Calcium chloride jar.
E. Tapered clay and rubber connector for the charging end of the tapered combustion tube.
F.
G Electric combustion furnace.
H. Jar for granular zinc to remove
  Acid fumes,
  Litharge fumes,
  Sulphur fumes,
  Chlorine fumes.
I. Jar for phosphoric anhydride to remove water.
J. Absorbent and weighing apparatus for carbon dioxide.
K. Guard tube—not to be weighed.

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* Reprinted from the Journal of the American Chemical Society (with additions), Vol. XXX, No. 5, May, 1908.

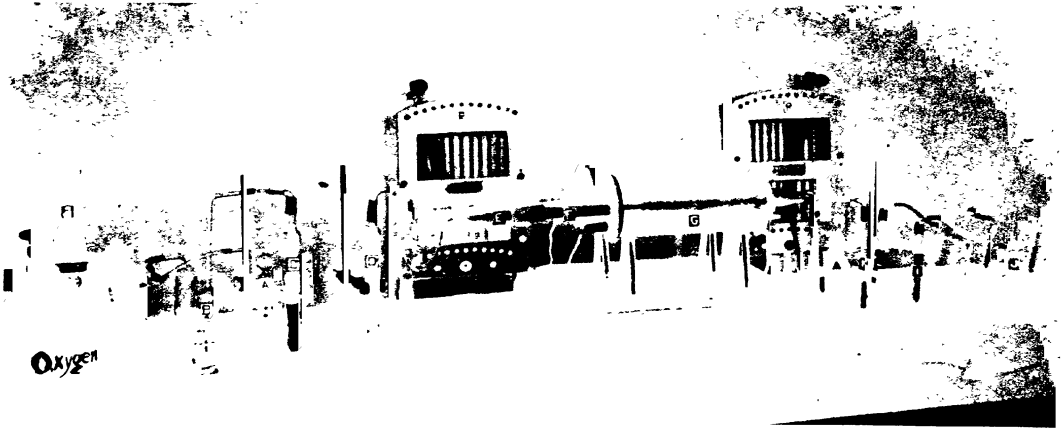

Photo No. 7.

Photo No. 8, page 278 illustration No. 14, shows the author's furnace as he built it when ni-chrome wire could be bought without also paying a yearly license on all devices into which it is put, in addition to the price of the wire; No. 1 in this photo is the mercury pressure gauge; No. 2 the KOH safety jar; No. 3 contains stick KOH, No. 4 contains anhydrous calcium chloride; No. 5 shows the rubber sleeve connection at the charging end of the tapered combustion tube of zirconia composition; No 7 shows the author's design of furnace with the solid white casing of infusorial earth consisting of a split cylinder; No 8 is his zinc jar; No 9 is the P_2O_5 jar; No. 10 is his KOH absorption and weighing apparatus and No. 12 is a little guard tube filled with small pieces of dry KOH This guard tube is not weighed The weighing apparatus is shown drawn to scale in illustration No. 15.

At that time the writer put in a small 32-ohm rheostat that happened to be at hand, and with about one-fourth of this resistance the furnace, on a 220-volt direct current, maintained a constant temperature. To secure complete combustion of steel it is very essential that the heat be maintained as close to 980° to 1000° C. as possible, i.e., as little under that temperature as practicable. If the temperature drops to about 900° or under, the results obtained are liable to be from 0.01 to 0.10 per cent too low, unless red lead is mixed with the drillings. Hence, if one desires to operate with oxygen alone, the necessity of keeping the temperature from 980° to 1000° C. cannot be made too emphatic.

The oxygen is purified by passage through jars of stick caustic potash, potassium hydroxide solution, calcium chloride in the order named. The oxygen then passes into the quartz (fused silica) or clay tube, half of which is filled loosely with ignited asbestos. The products of the combustion are purified from acid sulphur, litharge or chlorine fumes by passing through a jar of granulated 30-mesh zinc. The water is removed by a jar of phosphoric anhydride.

For steels containing from 0.30 to 1.50 per cent carbon 1.3636 grams of fine drillings, not over $\frac{1}{4}$ mm. thick are taken. For still lower percentages of carbon 2.727 grams of drillings of not over 20-mesh size are selected.

The sample is weighed into a clay boat. The steel begins to burn by the time the stopper of the combustion tube is in place. One gram of steel is decarbonized in three minutes and 3 grams in six minutes. The burning is continued for ten minutes more

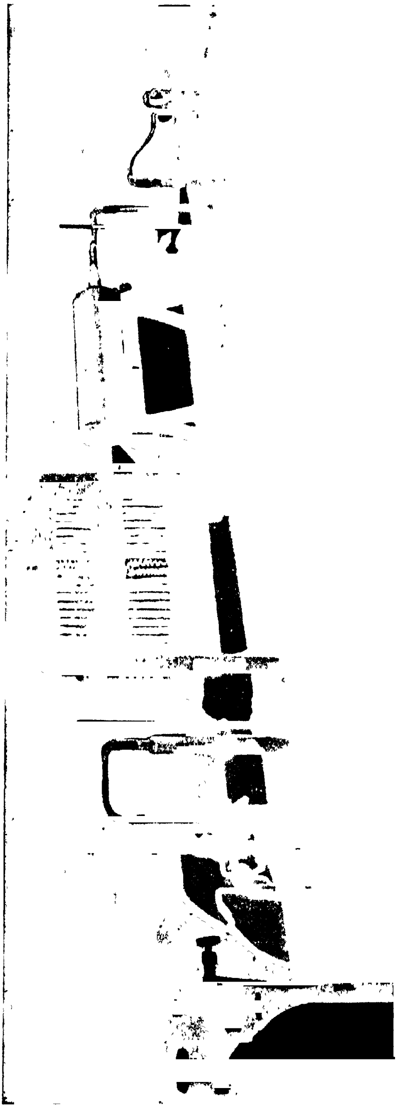

PHOTO NO. 8. ILLUSTRATION NO. 14.

with oxygen passing through the combustion tube at a rapid rate. The weighing apparatus is detached, wiped and weighed. Twenty minutes afford ample time for a single combustion, counting all operations.

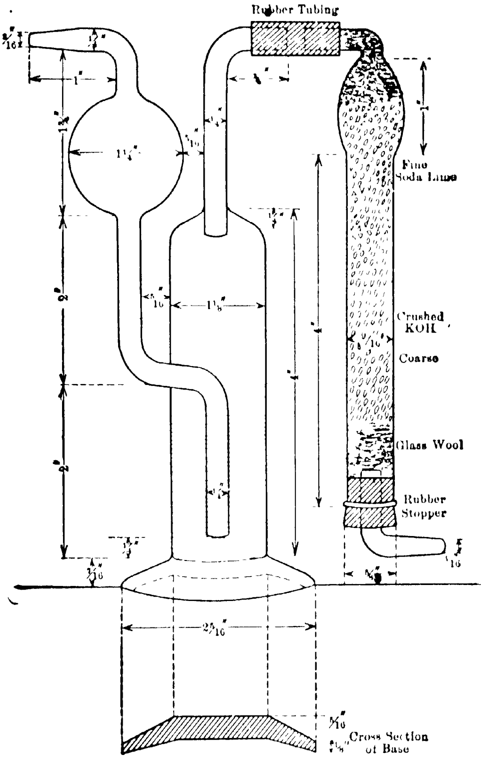

ILLUSTRATION NO. 15.

The weighing apparatus and the jars for the purifying train are the author's design, and were first published, in part, with illustrations, in the January *Journal of the Engineers' Society of Western Pennsylvania*, 1906, and more fully in the *Journal*, Am. Chem. Soc., XXVIII, 862 (1906).

While no red lead is necessary for steel combustions, some of the alloys, such as ferro-chrome, carbonless chrome and ferro-boron, require that red lead be mixed with the drillings or powder to break the metallic bond and permit of decarbonization. Ferro-chrome is the most refractory, as from a carbon content of more than 4 per cent only 0.2 per cent was obtained by burning as in steels with oxygen alone, at a temperature of 940°. Pig iron also requires some red lead.

A few of the many comparisons made in this laboratory between the combustions in a gas furnace with red lead and oxygen and combustion in oxygen alone are given in Table I:

Sample	Method	Weight of Drillings Taken Grams	Amount of Red Lead Used	Per Cent Carbon Found
No 1 Steel	Electric	4	None	0 09
" 1 "	Red lead	4	7 grams	0 09
" 288 "	Electric	2	None	1 176
" 288 "	Red lead	2	4 grams	1 175
" 2 "	Electric	5	None	0 121
" 2 "	Red lead	4	7 grams	0 111
" 3 "	Electric	1½	None	0 976
" 3 "	Red lead	1½	4 grams	0 967
" 4 "	Electric	3	None	0 109
" 4 "	Red lead	5	7 grams	0 118
" 5 "	Electric	2	None	0 469
" 5 "	Red lead	2	4 grams	0 474
" 6 "	Electric	2	None	0 736
" 6 "	Red lead	2	4 grams	0 737
" 7 "	Electric	3	None	0 118
" 7 "	Red lead	4	7 grams	0 117
" 8 "	Electric	2	None	1 17
" 8 "	Red lead	2	4 grams	1 168
" 9 "	Electric	2	None	1 15
" 9 "	Red lead	2	4 grams	1 16
" 10 "	Electric	5	None	0 046
" 10 "	Red lead	4	7 grams	0 040

The advantages of the electric heating apparatus are obvious. Very little heat is radiated; economy of space is attained; tubes are heated gradually and cooled gradually; time required is the minimum; labor cost is plainly the lowest because of sim-

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Or litharge.

plicity and rapidity, and no expensive platinum tubes or boats or crucibles are used.

Some may say, "Why not burn the steel in air?" The answer is that the cost of oxygen is small, one-third cent per combustion, and the steel burns twice as fast in oxygen. Oxygen can now be had at 1¾ cents per cubic foot in 100 cubic foot cylinders. The method is accurate for all steels. As pointed out in the author's article and in his preliminary paper read before the Pittsburgh Section in December, 1905, one may lose as much as 50 per cent of the carbon in certain alloy steels by attempting to dissolve the borings in either neutral or acid double chloride of copper and potassium.

FERRO-ALLOYS AND PLUMBAGO

Sample	Method	Weight of Drillings Taken Grams	Amount of Red Lead Used	Per Cent Carbon Found
Tungsten powder	Electric	2	None	0.003
	Red lead	2	4 grams	0.010
Plumbago, No. 153	Electric	0.3	None	50.700
	Red lead	0.2	4 grams	50.800
Plumbago, No. 356	Electric	0.3	None	51.650
	Red lead	0.2	4 grams	51.300
Plumbago, No. 1	Electric	0.2	None	94.900
	Red lead	0.3	4 grams	94.300
68.5 per cent ferro-chrome	Electric	1.0	1 gram	4.21
	Red lead	1.0	4 grams	4.15
Ferro-vanadium, No. 131	Electric	1.0	None	3.12
	Red lead	1.0	4 grams	3.09
Ferro-titanium, No. 1	Electric	2.0	None	0.22
	Red lead	2.0	4 grams	0.24
Ferro-boron, No. 1	Electric	1.0	1 gram	1.73
	Red lead	1.0	4 grams	1.72
Carbonless chrome, No. 9	Electric	1.0	1 gram	0.08
96.0 per cent chromium	Red lead	1.0	4 grams	0.09
Pig iron	Electric	1.0	None	3.20
"B" .	Electric	1.0	0.5 gram	3.58
	Red lead	1.0	4 grams	3.58

The best protection for the bottoms of clay or porcelain boats is a liberal layer of ignited crude zirconia (zirkite).*

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* Read page 292 concerning the use of sand in combustion boats.

To secure complete decarbonization it is necessary either that thin drillings be used, or if the sample contains much coarse or bulky material, it should be selected. This can easily be accomplished by pouring the borings on a 20-mesh sieve and shaking all of the steel of 20-mesh size and the still more finely divided dust on to a 60-mesh sieve, which retains only the 20- to 60-mesh material. This *always* represents a good average sample.

Further, the drillings should be placed in as compact a mass as possible. If curly drillings are scattered along the entire length of the boat instead of being put in a deep, compact body, borings that are a little thick will frequently be found to still contain unburned metal. This detail is a very important one. Of course, the reason is that drillings lying in close contact, heat each other to incandescence during the burning with oxygen.

Also, during the period when the oxygen is being absorbed in large quantity by the burning metal, the flow of the gas should be regulated so that there is an excess. That is, the oxygen must be turned on in sufficient quantity so that the gas is bubbling through the weighing apparatus slowly.* However, if the gas is rushed through *J* during this period the steel becomes violently heated and slags with the sides of the boat, destroying the latter. Worse yet, low results are obtained frequently in this way, probably due to the formation of carbon monoxide, which is driven out of the hot portion of the tube before it is oxidized to the dioxide, or the slagging over of unburned steel.

If the oxygen is turned into the tubes in sufficient quantity to maintain a slow stream during the period of the burning, the end point of the combustion is distinctly shown by a sudden increase of the speed of the bubbling through *J*. The rush of oxygen is then checked, but the rate of flow is still rather rapid for the final ten minutes. (Photo 7, page 276.)

The weighing apparatus *J* (Illustration No. 15) is filled not quite to the bend of the inlet tube with a solution of potassium hydroxide made by dissolving 500 grams of the latter in 500 c.c. of water. The drying tube at the outlet of *J* is closely filled

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In order to maintain the slow bubbling through *J*, it is necessary to increase considerably the rate at which the oxygen is passing through *B* during actual burning of the metal to oxide. This also generates the required white heat in the steel at the critical time. See page 276.

with pieces of stick caustic potash cracked to about the size of a grain of wheat and a layer of soda lime above the KOH. To prevent the caustic potash from coming in contact with the small rubber stopper in the drying tube a *loose* plug of asbestos or glass wool is placed at that point. The little bulb of this drying tube is filled about half full of glass wool. If dry sticks of caustic potash are cracked quickly, the small pieces can be conveyed to the drying tube in dry condition and constitute not only a splendid guard against loss of moisture from *J* but are also equally effective as an absorbent of carbon dioxide.

The zirconia composition, 15×75 mm., boat is the best shape and most durable of any boats that the writer has tried.* When putting in the ZrO_2 bottom, fill the front half of the boat about two-thirds full and then with the butt end of the forceps make a trough in the ZrO_2, working it well up the sides of the boat. Pour the drillings from the weighing bottle into this depression. By so doing the drillings are kept in a compact mass, and when the combustion is completed the burned steel can be lifted out in a small cake. In this way a boat can be used many times.

When a great many combustions are made daily, the zirconia tube is the most serviceable. The continuous spraying of oxides against the walls of a porcelain tube weakens it, and when the current is turned off and the tube is permitted to get cold the contraction causes a rupture. Avoid spilling steel in a quartz tube. Tapered tubes are the best.†

To prevent the contents of *D* and *C* from clogging the inlets and outlets, large plugs of cotton are used at these points. Glass wool plugs should be used in *H* and loose plugs of ignited asbestos in *I*. The inlet end of a quartz tube heats somewhat, and it is better to wrap it several times around with a strip of cheese-cloth, the end of which dips into a 150 c.c. beaker of water suspended directly underneath by means of copper wire (see page 293.) During the absorption of carbon dioxide the outlet of *J* is protected from ingress of moisture or carbon dioxide or fumes from the room by a drying tube *K* shown in Photo No. 7, page 276. It is filled with pieces of stick caustic potash broken to the size of a pea. No wet wrappings are needed with tapered clay tubes.

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* These boats are now in general use.

† Read page 294 concerning the vitrified zirconia-composition combustion tube designed by the author.

Oxygen can now be had, under high pressure, in 50-foot cylinders at about 2 cents per cubic foot, and in 100-foot containers at about 1¾ cents per foot. The latter quantity will supply two furnaces, night and day, for two months. (1914.)

Gas Combustion Furnace with Blast.—The gas combustion furnace, described by the leading supply houses as "for draft or blast, with adjustable flame length" can be made very effective where compressed air is at hand. The author modifies it as follows: From the 450 mm. size take out one pair of tiles; shove the other two pair together into the middle of the furnace frame. Put the removed tiles on top of the remaining four to lessen radiation of heat. Close all of the burner shutters except the four middle ones. Let the inlet end of the ¾ inch inside diameter, 30-inch electro-quartz tube project 12 inches beyond the tiles, and the outlet end 6 inches beyond the tiles. Fill the latter end, *loosely*, with ignited asbestos for a distance of 8 inches, beginning at the stopper. Wrap both ends at the stoppers with wet cheese-cloth. It is essential that the combustion tube be at least 30 inches long, and either of electro-quartz or platinum, as with air blast and gas the furnace will heat the tube to 1000° C. in twenty minutes.

THE DIRECT DETERMINATION OF CARBON IN STEEL, FERRO-ALLOYS AND GRAPHITE BY MEANS OF A COMPRESSED AIR AND GAS FURNACE

Compressed air should be considered a necessity in all chemical laboratories, however small, where ignitions of any kind are part of the daily routine. With this great aid to combustion the furnace shown in the illustration (Fig. 16) can be made to heat a ¾-inch bore fused silica tube to from 1150° to 1200° C. in from fifteen to twenty minutes. The cut shows the writer's modification of the original arrangement of the tiles. One pair of the latter is removed from a 495 mm. furnace; * the other two pair are shoved together into the middle of the furnace. The removed tiles are placed on top of the middle pair forming an arch at *P*, *P*.

The vacant spaces at either end of the frame are packed with asbestos wool. All of the burner shutters are kept closed except, the four middle ones at *O*. To permit the flame to pass up freely,

* No. 17 furnace, 18 inches long.

the tiles are separated about ¾ inch at the bottom, *M''*, *M'''*, and ¼ inch at the top, *M*, *M'* (Fig. 16). This is easily accomplished by sliding one-half the iron frame up the inclined iron supports. One can readily adjust the air pressure and the gas at the points indicated to produce 950° C. in ten minutes. The range between 950° and 1000° is best for the work. To provide for variations of air pressure a small regulator is located at *R*. This regulator is inexpensive and can be bought from any concern supplying pressure faucets.

To prevent the cracking of the fused silica (electro-quartz) tubes when using this furnace for the determination of carbon in steel by the direct combustion of the drillings in oxygen, a small inner sleeve or tube of platinum or nickel should, by all means, be at hand. If the quartz combustion tube be heated much above 950° C. and a single drilling is spilled in it, or the highly heated steel cuts through the clay or porcelain boat, the oxide of iron forms slag with the silica of the tube and the latter will soon crack. To avoid frequent and expensive breakage of combustion tubes from this cause the writer, in 1906, designed the small cylinder of platinum shown at *Q*, *Q'* (Fig. 16). *Q* shows the open end of the same and *Q'* gives a view of the closed end of the cylinder. One-half of this end is perforated with small holes. It is 125 mm. long and 18 mm. in diameter. It can be made to weigh not over 30 grams and at a cost of about $28.00,* at that time. The cylinder is kept in the combustion tube. To receive the charged boat and for the removal of burnt residues this holder is drawn nearly but not quite to the entrance of the

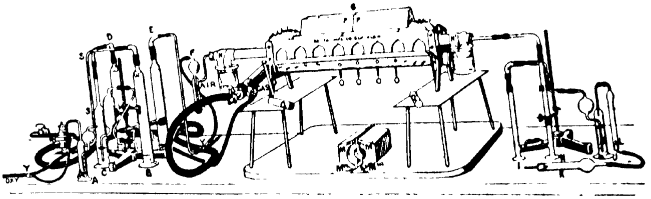

FIG. 16.—Showing the Fletcher Tube Furnace as Modified by the Author and fitted with his Combustion Train

quartz tube. Keep it just a little back of the stopper. The clay boat into which the steel drillings are poured, in a little pile, is slipped into the cylinder and the combination is quickly pushed into the hottest part of the combustion tube. The tube is stoppered as rapidly as possible and oxygen is immediately turned in with sufficient volume to maintain a medium rate of bubbling through the absorbing and weighing apparatus *J*. As soon as the steel gets heated, it begins to absorb oxygen in large quantities as shown by the slackening of the rate of bubbling through *J*. It is highly important to continue to turn in more of the gas so as to always maintain an excess of it or low results may be obtained. Increase the flow of the oxygen through *C* so as to keep up a fairly rapid stream of gas passing through *J* during the absorption period. When the burning is completed, which occurs in about five minutes after the tube has been stoppered, the oxygen will begin to rush through *J* at a high rate of speed. The flow is now checked to the normal, which is still quite rapid, as but ten minutes more are allowed to complete the combustion of 2 grams of steel and carry all of the CO_2 over into the weighing apparatus *J* (Fig. 16). Allowing two minutes for the final weighing, an accurate combustion of steel drillings can be made in from twenty to twenty-two minutes. The writer operates furnaces in pairs by a two-way connection. This still further reduces the average time per combustion, counting all operations except the drilling of the sample.

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* The present high price of platinum makes this cylinder undesirable, a clay cylinder could be used in 1 in. bore tube.

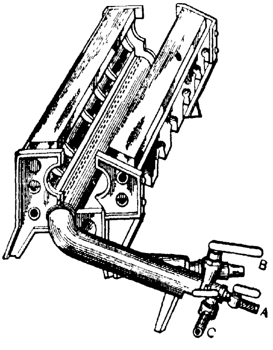

Fig. 17.—No. 17 Furnace Open Ready for the Introduction of a Tube.

The second furnace is placed parallel with the one shown in the cut. The air pressure for this extra furnace is bled from a cock on the furnace, shown at *A* (Fig. 17). It is the middle one which is closed in the illustration (Fig. 16). The air is conducted from this point to the same cock on the additional furnace by heavy pressure tubing. In this way air for two furnaces can be supplied from one regulator at *R*. By similar means, through a *Y* not given, gas can be furnished from the one gas nipple located near *R*.

The oxygen is turned in at *oxy* (Fig. 16) and is distributed at the first *Y* to the pressure gauge at *A* which contains a little mercury. It serves the two-fold purpose of indicating stoppages and leaks. If there be a stoppage, the mercury will rise to an abnormal height in the tube that dips under the mercury in *A*.* To test for leaks, plug with a glass rod the outlet end of the purifying train at the point where the absorption and weighing apparatus *J* is shown attached. Then turn on the oxygen until the mercury rises in *A* to the first bend of its outlet tube. Then shut off the oxygen. If there be a leak beyond *C* in the direction of the furnace, the mercury will slowly drop and the slightly compressed oxygen will bubble very slowly through *C*, if the leak be a small one. But, if the leak be somewhere between *C* and the oxygen tank in the direction *BS'S*, then instead of there being a bubbling through *C*, the fluid in the latter will recede from the bottom of *C*, rising up into the side bulb of *C*. The valves on oxygen tanks frequently develop leaks and the little gauge at once calls attention to the fact if this test is made. *C* is filled to the distance shown in the drawing with a solution consisting of 250 grams of caustic potash dissolved in 250 c.c. of distilled water. The oxygen, after passing the first *Y*, enters *B* via the glass tube *SS*. It then passes down through *B* (Fig. 16) which has a loose plug of cotton at the top and is filled with short pieces of stick caustic potash. The gas leaves *B* at the bottom outlet and enters *C* via the S-shaped glass tube. The gas bubbles through the fluid in *C* and enters *D* at the top where there is a loose wad of cotton. *D* is filled with alternate layers of anhydrous calcium chloride and cotton. The gas leaves *D* at the bottom outlet and enters *E* at its bottom inlet. *E* is filled with alternate layers of cotton and soda-lime. The bottoms of the jars are filled with loose plugs of cotton to prevent the clogging of inlets and outlets by these salts. The oxygen travels up through *E* and, by way of a glass tube, can be distributed to the pair of combustion furnaces at the second *Y* tube.

The combustion tube is of fused silica, or electro-quartz. It is 30 inches long and projects 12 inches beyond the furnace frame at the inlet end and 6 inches beyond the frame at the outlet end. It is filled loosely with ignited asbestos for a distance of 8 inches beginning at the outlet end. Both ends of the tube are wrapped at the stoppers with wet cheese-cloth, the ends of which dip into the beakers filled with water as shown at *N*, *N'*. The products of the combustion are purified from litharge, sulphur, chlorine, and acid fumes by a jar of granulated zinc of 20-mesh fineness (*H*). The gases are further dried by passing *up* through a jar of P_2O_5 powder (1). "1" has a loose plug of ignited asbestos at the bottom of it and a similar one at the top. The pure CO_2 is now received into the weighing apparatus *J* which is filled with the same kind of solution as given for *C*, halfway to the bend of the tube that dips into it. The guard tube *L* is filled with small pieces of dry caustic potash prepared by quickly breaking the dry sticks in a porcelain mortar to about the size of large grains of wheat.* Reject the dust and use it for the absorbing solution. Such a tube makes a most effective guard against loss of moisture from *J* and also acts as a further absorbent of CO_2. This apparatus *J–L* is good for forty ordinary steel combustions at a rapid speed. It is weighed against a mate and thus eighty combustions are obtained from a pair before refilling is necessary. *D*, *B*, *E*, *I*, and *H* are refilled by removing the glass goose necks. The tube *K* is filled with the same material as *L* and prevents any suction of impure air into the weighing apparatus during the process of a combustion. The author designed the entire train several years ago with a view to reducing the use of rubber stoppers to a minimum and to provide a convenient form of weighing apparatus for carbon dioxide. When using *J–L* for the determination of carbon in plumbago (natural graphite) it is replenished when 3 grams of CO_2 have been absorbed.

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* When two furnaces are in operation the required pressure in *A* will cause the mercury in it to rise to a height of about 35 mm. It is a great advantage to have two furnaces. One checks the results obtained in the other

It is important that the small tube that dips into the KOH solution in *L–J* be not less than 6 mm. outside diameter and that its internal diameter be not reduced as it is very necessary for rapid work that it deliver large bubbles to the absorbing fluid.

In ordering quartz or fused silica tubes the chemist should specify that the ends be fused smooth, free from inside chipping and grooves, and of practically round bore, otherwise he may have unpleasant experiences with leaks at stoppers. He should further insist that the tubes be of full ¾ inch inner diameter for at least three-fourths of the length, or his small protective cylinder may stick in the tube.

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* The bulb of *L* is filled with glass wool. The little rubber stopper is protected from the pieces of KOH by a loose wad of ignited asbestos.

Care should be taken to keep the heat of the furnace very little in excess of 1000° C. as combustion with oxygen at higher heats will cause the drillings to flux with the boat, cut through the latter, and at times stick to the protective sleeve. The operator will soon learn to judge the proper heat without a pyrometer. If on drawing out the boat he finds nothing in it but a fused slag and that, perhaps, the latter has cut through the boat, then he has been working at a temperature in excess of 1000° C. If he finds a residue that is a dull black mass of oxide which can be broken off short in his fingers, does not present more than a slight melted appearance on top and does not contain particles of unburned steel, then the temperature of the furnace is just right. If the residue instead of being of a dull lustrous jet black has a slightly reddish appearance, the combustion has been made at too low a heat and the decarbonization is incomplete. If the combustion tube presents a white hot appearance, inside, the heat has attained to 1200° C. If the heat has a dazzling effect the temperature is still higher. A yellow heat, viewed in the bright daylight, is about 950° to 980° C.; a bright yellow, suggesting the first appearance of whiteness, is about 1150° C. By exercising a little care in adjusting the air and gas supply this furnace can be operated with very little noise or radiation of heat and yet develop from 980° to 1000° C., which is ample for direct combustion of steel in oxygen. A small milling attachment should be on every drill table, such as is used in "gumming" saws. In this way finely divided millings can be obtained from thin sheets, wire and razor blades. The author used one-eighth pitch cutters that were held in a chuck in the same manner as a drill. The sheet or wire is clamped to the drill table and is shoved against the milling cutter which is revolving horizontally. The author now uses his milling machine (see page 271, Fig. 9).

The drillings or millings, which should be either very thin, medium size, curly ones or should pass a 20-mesh sieve if from soft or annealed steel, are put in the boat in as compact a mass as possible. The drillings should not be scattered. Do not try to remove the residue after a combustion. Put in the next sample in a little pile and as close as possible to the oxide remaining from a previous analysis. In this way many carbon determinations can be made in a zirconia boat without bothering with a sand bottom. Of course porcelain boats can be used for this work but they are more expensive and do not last as long as a well made clay boat. Zirkite should be used to protect the bottoms of the porcelain boats. As stated the author has found that, with a little practice in manipulation of the gas and air pressure, the furnace shown in the cut can be made to heat to from 980° to 1050° C. with very little noise and radiation of heat. On the other hand it can be run with much unnecessary racket. In this laboratory natural gas is used at a pressure of 8 ounces. A moderate air pressure is sufficient, i. e., about 30 pounds.

When making direct carbon combustions of pig iron in oxygen, shake up with the 1 gram of sample half this amount of red lead or litharge to break the bond between the iron and silicon. This secures complete combustion of pig iron. For refractory substances like ferro-chrome, carbonless chrome, silicon carbide, metallic silicon and ferro-boron, weigh 1 gram of sample and mix the same with 4 grams of litharge. Put this charge in a clay boat and proceed with the combustion as given for steels. Deduct a blank due to the CO_2 obtained from the lead oxide. It is safer to follow this plan for tungsten and molybdenum powders, ferro-silicon, ferro-vanadium, ferro-titanium, and ferro-molybdenum. All varieties of plumbago or natural graphite that the author has analyzed in connection with the plumbago crucible factory of this works, when finely ground as described in his methods for the analysis of graphite, burn completely to CO_2 in oxygen. Some of the finer grades of the natural concentrated product yield 99 per cent pure carbon. It requires about forty-five minutes to completely burn such material.

When using red lead or litharge to secure complete combustion of the carbon in ferro-alloys rich in aluminum or silicon, or both, the charge is placed in one end of the clay boat, *without* a sand bottom. After completing the combustion which proceeds just as quickly as that of a steel with oxygen, alone, the used part of the boat is broken off and the other half is then taken for further combustions. The best way to determine the blank, due to the lead oxide, is to burn 2 or 4 grams of it with some 20- to 30-mesh siftings of a steel, the carbon content of which is accurately known; or with 2 grams of small thin curly drillings of some standard steel. The excess of carbon found is the blank due to the lead oxide. A good c. p. or commercial red lead or litharge will give a blank of about 0.004 gram of CO_2 per 4 grams of lead oxide.

L–J is wiped off with a piece of clean cheese-cloth or a clean handkerchief before each weighing of it. Its outlet and inlet ends are kept closed with small rubber caps when it is not connected in the train. These caps are removed during weighings. Not more than two minutes are spent in weighings at the end of the combustion. One minute is sufficient to weigh the drillings at the start. One or two minutes more may be consumed in transferring the boat to the combustion tube and connecting *L–J* in the train. But fifteen minutes are required to burn the sample and carry all of the CO_2 to *L–J*. In this way perfectly accurate combustions of all kinds of steels, either plain or alloyed, with any amount of tungsten, molybdenum, or chromium can be carried through in twenty minutes. This is the routine practice in this laboratory when making bath tests of open-hearth heats before same are ready for tapping.

This furnace has one marked advantage over electrically heated furnaces, in that it can be brought from a cold state to 1000° C. in ten minutes. It can also be adjusted to fit any size combustion tube. (See Fig. 17.)

Rapid Bath Test for Carbon by Combustion.—Weigh 1.3636 grams of 60-mesh or thin curly drillings into a clay boat. Place the boat in the combustion tube heated to 1000° C. Pass the oxygen at a rapid rate—three bubbles per second for five minutes. Continue this burning for five minutes more. Detach the absorbing and weighing apparatus, No. 10, Photo No. 8, page 278, and weigh.

CHAPTER XI

PART III

FURTHER NOTE ON THE DETERMINATION OF CARBON IN STEEL AND FERRO-ALLOYS

Surface Decarbonization.—Referring to remarks on page 268 relative to the taking of samples it must be noted that steel often has a decarbonized surface, that is from 10 per cent to almost any amount lower in carbon than the main body of the metal. This will often cause the chemist to report the rolled or hammered steel anywhere from 0.10 to 0.20 lower in carbon than the original ingot analysis, that is, suppose the ingot analysis was 1.20 per cent carbon, then it not infrequently happens that the plate or bar may show but 1.10 per cent.

Use of Sand in Boats.—The author no longer uses any sand in the combustion boat as the composite vitrified clay boat is greatly superior and withstands a much higher heat than the original form of clay boat. By avoiding extreme heats during the combustion, complete decarbonization can be effected without fusing the drillings to the boat, and the little pile of sintered oxide that remains after the burning can be scraped out with the tail of a small file. If the combustions are run at a high heat with the drillings in contact with a sand bottom there is danger of forming silicon carbide as has been pointed out by Mr. Geo. M. Berry. Crude ZrO_2 or chrome ore are good boat protectors.

Oxygen Versus Air in Direct Combustion.—Since writing the first edition of this book the price of oxygen has fallen to less than two cents per cubic foot, so that there is no longer any inducement to try direct combustions in air. In any case the high temperatures necessary make such combustions very unpleasant and should be avoided.

Two Parallel Furnaces.—Photo No. 18 shows the author's arrangement for two combustion furnaces, side by side, when

PHOTO No. 18.

quartz tubes are used. Note the wet wrappings required when quartz is used.

The Gas Combustion Furnace with Blast.—On page 284 the above direct combustion method is referred to. It constitutes a very cheap and effective way of making direct combustions. The principal objection to this method of heating is that the sharp, bare flame of the compressed air furnace striking the fused silica tube causes the latter to become devitrified and leak after some time.

THE ELIMINATION OF RUBBER STOPPERS FROM THE VITRIFIED CLAY COMBUSTION TUBE BY MEANS OF TAPERED CLAY INLET AND OUTLET *

In June of 1913 the author published an account of a vitrified clay combustion tube with tapered outlet designed by him. These tubes are now widely used.

The advantage of the tapered outlet very soon suggested the making of a tapered clay inlet which is shown at *K* in the illustration and also at *L–M*. (Fig. 19.)

The clay part of the inlet is a duplicate of the outlet end. The tube is charged and discharged by removing *L–M* which is connected to the main part of the combustion tube by means of the rubber sleeve *M*. This connection is a piece of $\frac{3}{4}$ inch bore, $\frac{3}{16}$ inch wall and $2\frac{1}{4}$ inches long, pure rubber tubing. This sleeve is more easily handled than a rubber stopper. The operator grasps *L–M* at the clay part *L* and slips it over the main part of the combustion tube and twists it firmly in place. The clay part *L* offers a substantial hold for one's hand and is absolutely safe. A glass taper would be dangerous as it might be crushed when grasped, causing a wound.

The slip-over connection is geometrically a tighter connection than a rubber stopper, for the reason that the latter affords an example of a conical surface pierced by the cylindrical surface of the combustion tube, which makes only a single circle of contact between the stopper and the tube. The slip-over gives a tangential contact which provides innumerable circles of contact.

Further superiority of the tapered clay and rubber sleeve inlet is that, should the bore of the combustion tube tend to

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* Reprinted from Journal Ind. and Eng. Chem., V, 488.

PHOTO No. 18.

be elliptical instead of a true circle, the elasticity of the rubber sleeve will still give a pressure tight connection on account of the large surface of contact.

Again, many combustion tubes offered by dealers are rejected because of grooves in the interior walls, at the inlet or outlet ends, which make tight connections with rubber stoppers impossible. The tapered slip-over connection renders such tubes perfectly satisfactory.

The entire apparatus with the single exception of the little mercury valve tube attached to *L–M* is the author's design and shows but one rubber stopper at an unimportant point in the little KOH drying tube at the extreme outlet end of the combustion train. This could also be eliminated by a small glass taper or clay taper. The wet wrapping can be omitted, entirely, when the clay tube is used, although shown in Fig. 19.

It has been found in the author's experiments that, for a given wiring, furnaces heat higher with clay tubes than when fused silica tubes are used as there is less leakage of heat via the tube when the clay tube is in the furnace.

CHAPTER XI

PART IV

THE DETERMINATION OF CARBON IN PLAIN STEEL AND IN ALLOY STEELS, CONTAINING NOT OVER ONE OR TWO PER CENT OF ALLOYS, BY SOLUTION IN COPPER AND POTASSIUM CHLORIDE

THE limitations of this method cannot be absolutely fixed as the carbon can be accurately obtained on certain alloys that have a greater amount of the non-ferrous metals than given in the above title; notably nickel steels can be accurately determined for carbon where the nickel content is far in excess of 2 per cent. The reader should refer in this connection to pages 257 to 260. Occasionally the chemist receives thick chips that are impossible by the method given on the pages just mentioned, and rather than wait for a more suitable sample or perhaps put a good customer to the inconvenience of getting drillings of the proper fineness, the analyst will resort to the double chloride method. The details are as follows:

The Dissolving Solution.—The acid solution given on page 258 is used for this work. It is filtered on ignited asbestos. The latter is prepared by igniting the fine white fiber in a muffle furnace in a porcelain dish. The dish is filled heaping full and brought to a bright red; it is then removed from the furnace and allowed to cool below redness. The lump of partially ignited asbestos is turned over and the dish and its contents are returned to the furnace; again brought to bright redness; and so on until the asbestos has been heated and cooled three times. While the asbestos is cooling it should be covered with a clean agate ware pan to prevent soot or carbonaceous dirt of any kind from falling on the asbestos. The ignited asbestos is cut into short wads; put into a glass stoppered, carefully cleaned quart bottle and enough distilled water mixed with it to make a rather thick pulp.

The pulp is poured on a perforated porcelain plate of at least 2 inches diameter which is kept from slipping out of level by applying slight suction while the filter is being prepared. The asbestos is distributed over the plate in an even layer about 1 inch thick and is put firmly to place by increasing the suction a little and pressing it down with a glass rod. (One end of the rod is flattened into a disk by softening it in the flame of a Bunsen burner and quickly pressing it against a cold surface.) Repeat this operation, adding, in the same way, successive layers, taking care not to tamp the latter too much, as by so doing the filtration will be very slow and will require excessive suction to get the solution through the filter at all. When the layers have attained a total thickness of about an inch and one-half the whole filter is saturated several times with 1 : 1 HCl to shrink it tighter; it is tamped some more, and then washed ten times with distilled water. The glass filter * tube in which the filter is made is

FIG. No. 20.

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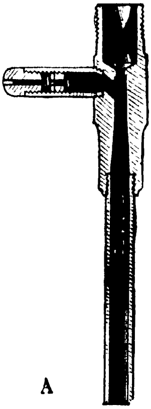
* The filter tube shown in Fig. No. 20 contains a rubber gasket and alundum thimble; these are removed and a perforated porcelain plate is substituted for the carbon filtration.

shown in Fig. No. 20. The filter being now ready is transferred, rubber stopper and all, to the bottle in which the solution to be filtered is to be kept. The photo shows a glass filter tube, but usually a carbon filter tube is too small for filtering the whole solution so that the filter layer is prepared on the porcelain plate supported in a large funnel that pierces a rubber stopper that will fit the neck both of the side neck suction flask shown and of the large glass stoppered bottle in which the filtered solution is to be preserved. The double chloride is then filtered into the latter bottle with moderate suction; kept stoppered; and, to prevent dust from settling around the stopper, a cap of stout paper is tied over the same. The Fig. No. 20 shows the brass water pump used which is extremely satisfactory and inexpensive. It discharges into a deep stone box as shown. Cut A illustrates the details of the brass pump.


A

Solution of the Chips and Filtering Out of the Carbon.—Dissolve from 1 to 5 grams of the chips in 60 c.c. of the double chloride per gram of sample in a beaker that has been cleaned from all lint or dust. The chips must be stirred at intervals with a glass rod until there no longer remains on the bottom of the beaker any particles of copper-coated steel. The reactions occurring are given herewith for the benefit of the student: In the first place the iron is dissolved away from the carbon by reaction (1), $Fe+CuCl_2=FeCl_2+Cu$; then a further portion of the copper chloride in the double chloride solution causes the metallic copper formed to pass into solution in the manner shown in reaction (2), $CuCl_2+Cu=2CuCl$. This cuprous chloride ($CuCl$) would form and separate out as a white precipitate were it not for the excess of acid present in the double chloride which excess of HCl dissolves the cuprous chloride; hence it is best to wash the carbon residue on the asbestos filter at first with some of the double chloride before washing it with water.

The carbon is filtered on an asbestos filter supported on a perforated porcelain plate just large enough to fit in a glass carbon filter tube of 1½ inches diameter. This filter is prepared in exactly the same way as described for the larger filter used for the double chloride. A row of four of these carbon filter tubes are shown in Fig. No. 20. The well-tamped and acid shrunken layer of asbestos need not be over ½ inch thick. The dissolved chips are poured through the asbestos filter and any black particles of carbon adhering to the walls of the beaker are best discovered by holding the latter over a sheet of white paper. These particles are transferred to the filter by rubbing them loose with a rubber-capped glass rod, rinsing the beaker with a fine jet of water and also some of the double chloride. The carbon being now all on the asbestos it is washed five times with some of the double chloride, drawing off each washing with mild suction. The acid is then carefully removed by giving the filter thirty washings with distilled water, drawing off each one entirely before the next washing is applied. The carbon filter tube is then withdrawn from the rubber stopper. The porcelain plate with its adhering asbestos and carbon is carefully pushed out of the filter tube on to a clean watch glass, with the plate side down. Any carbon sticking to the walls of the filter tube is completely removed by wiping them off with some of the asbestos. The top part of the asbestos filter is first stripped off and placed in the clay combustion boat. This leaves all of the rest of the filter to be used in cleaning out the filter tube. This portion of the filter is now moistened with water. A pair of steel forceps that are not too stiff are used to hold the portions of the dampened filter that are used for removing carbon that sticks to the filter tube. Then, at the last, the points of the forceps should be wiped off with a little of the pulp as some of the carbon is likely to be on the forceps. The operator should wash his hands before beginning the transfer of the carbon filter and the cleanings to the clay boat. A piece of stout wire or a glass rod is used for pushing the plate and the adhering filter out of the filter tube. Dry the contents of the boat in a water or air oven for two or three hours. When dry, as shown by there being no noticeable condensation upon a cold watch glass placed over the boat immediately after the latter has been taken hot from the air bath, the contents of the boat are pressed firmly down into it and 4 grams of red lead are spread over the same. The boat is then placed in the electric furnace and the carbon is finished in the same manner as given for the direct combustion. The water should be dried out of the carbon residue in the boat at a temperature not exceeding 100° C. The blank is run by placing the same amount of the double chloride in a beaker; filtering it through a filter made as in an actual sample and putting this filter through all of the operations just described, including the red lead covering.

CHAPTER XI

PART V

QUALITATIVE TEST FOR GRAPHITIC CARBON IN STEEL AND IRON

POLISH the steel carefully free from all scale. Any finely divided scale left on the steel is liable to be mistaken for graphite in the qualitative test.

Take either millings or drillings from the polished sample, whichever are most convenient. Use the milling machine for thin sheets. Dissolve 100 mg. of the millings or drillings in 4 c.c. of 1.20 sp. gr. nitric acid. Heat in water bath for forty minutes in boiling water in a test tube 150 mm. long×16 mm. diameter, in the manner described for color carbon tests in steel. The boiling should be continued until all flakes of combined carbon are dissolved.

Remove the tubes carefully from water bath, avoiding all shaking up of contents. Hold each test tube over a sheet of white paper. Look down through the mouth of the test tube. If there is the slightest black sediment in the bottom of the tube, this indicates at least a trace of graphite. If there is no sediment, the steel can be pronounced free of graphite. If there is a heavy deposit, the steel contains a high percentage of graphite. The samples showing a trace, or more, of graphite can be determined *quantitatively* by the following quantitative methods.

0.10 per cent graphite makes a large showing by the qualitative test. 0.17 per cent or less can be seen in the fracture by the dark appearance it gives to the grains of steel.

In steels dissolve 3 or 4 grams of drillings in 60 c.c. of 1.20 nitric acid, boil slowly, avoiding the concentration of the nitric acid by adding a little water if necessary, until the flakes of combined carbon are dissolved. Perfectly annealed steel in which graphitic carbon is most frequently found, does not show this flake and the heating is continued until the main solution no longer continues to grow any clearer. This requires about ten minutes' boiling.

In pig iron 1 gram is dissolved in 20 c.c. of the above acid aided with 2 or 3 drops of HF, boiling ten minutes. The insoluble matter is filtered on the same kind of an asbestos filter as is described for carbon in steel where the chips are dissolved in the double chloride of potassium and copper. See page 297.

The residue on the filter is washed thirty or forty times with water to remove the iron; then with 1.1 specific gravity KOH solution which is made by dissolving 30 grams of KOH in 200 c.c. of water. The washing with the KOH is continued until the washings are no longer colored brown. Then wash with water as many times as before; then with 1 : 1 HCl to neutralize any remaining KOH; and finally again, thoroughly, with water. The graphitic residue is removed from the filter, dried, covered with red lead, and finished as described in the direct method for carbon in steel, in the electric furnace.

The filtrate from the carbon or graphite, in this method, or in the double chloride method, should be poured through a filter paper and washed free of color to note if any black stain remains on the filter; if there be such a stain then some of the carbon or graphite, as the case may be, has run through and the result will be too low.

Method for the Determination of Graphite in Steel Used by the Safety Razor Company.—Dissolve 3 grams of the steel in a 150 c.c. of dilute nitric acid. (3 parts of water to 1 part of concentrated nitric acid.)

After adding acid to the steel, boil until red fumes of nitrogen oxide are gone. Then add 15 c.c. to 35 c.c., i.e., an excess of potassium permanganate (5 grams $KMnO_4$ in a liter of water). Boil until $KMnO_4$ is all decomposed, which should show an excess of manganese oxide after boiling a few minutes, otherwise some combined carbon will be counted as graphitic carbon. Cool, then dissolve the manganese dioxide, which may be precipitated, with the smallest amount possible of SO_3 or $FeSO_4$; filter out any black insoluble residue on an asbestos plug. Wash well with water, being very careful that none of the residue runs through. Wash with water until free of acid. Pour the filtrate and washings through a 9 cm. filter and wash the paper. Note if any black residue ran through. If it did, the result will be too low, and a new portion must be started and a tighter plug used.

Remove this asbestos from the filter tube. Dry it at not over 100° C. until free from moisture. Burn residue in the clay boat in the carbon combustion furnace for thirty or forty minutes. Weigh CO_2 formed. Run blanks all the way through, using all of the reagents, filter on asbestos plug, wash the same as the test. Dry this plug; burn it off in a carbon combustion furnace, and any carbon dioxide found is deducted from the carbon dioxide found in the sample by the same method. Any carbon dioxide remaining is calculated to carbon. This carbon is called graphite

CHAPTER XII

PART I

CARBON BY COLOR

THE determination of carbon by color methods should be indulged in as little as possible. Numerous interferences render analysis, unless carried out under the guidance of persons of long experience, highly inaccurate. The heat treatment, i.e., the greater or less amount of *incidental* annealing that a sample may have had, will cause the color to vary, yielding results from 10 per cent to 20 per cent away from the actual carbon. The perfectly annealed steel, i.e., where the carbon has all been converted into the absolutely annealed condition, yields the greatest depth of color for a given percentage. A few tenths of a per cent of highly coloring elements like chromium give low results compared with a standard steel not containing the alloy. Also the presence of considerable manganese tends to lighten the color in unannealed steel. The same is true of nickel.

If a sample consisting of large, bulky, thick drillings be compared with a standard of small, uniform size, thin drillings, the bulky sample will yield results often 10 per cent too low. The presence of graphitic carbon will cause results to be anywhere from 5 per cent to 90 per cent too low. Of course, much graphitic carbon is easily detected by the insoluble black residue that remains in the solution so that only 5 per cent too low is likely to be unnoticed. A practiced eye will detect the slightest trace of it. If the operator can drill his own samples and always get them with the same heat treatment, and have a standard that has undergone the same treatment, and has been drilled with the same depth of cut, his results will be fairly accurate.

There are two means by which one may approach the ideal:

First. When the drillings to be tested and the standard drillings have been taken from the raw cast steel that has never been reheated and is always allowed to cool slowly from the molten state, i. e., without any quenching.

Second. Where the operator is furnished the steel and can anneal it to the last degree of softness, avoiding the temperature range most favorable to the formation of graphitic carbon (see Annealing of Steel). Then drill such samples to uniform thickness and compare them with a standard prepared in exactly the same manner. This second scheme is the most accurate of all color methods. For the identification of the perfectly annealed condition, see Annealing.

Further, it is essential in color work that the standard shall be within 10 per cent of the carbon content of the sample to be tested. The nearer the carbon of the standard is to that of the test, the better; especially is this true of unannealed steel.

Method.—Dissolve 100 mgs. of sample in 4 c.c. of 1.20 nitric acid. Use a test tube 152 mm. by 15 to 16 mm. diameter. Insist that the dealer supply test tubes that keep within the same diameter. If one test tube is wide and its mate narrow, the wide one will permit more of the free acid to escape than the narrow one, causing variation in the color. Do not set the tubes deep in the boiling water, as it will cause iron to dry on the sides, and, when this is redissolved by shaking the hot acid solution the brown basic nitrate of iron will go into solution, causing another variation of color.† The fewer tests dissolved at one time the better, as some parts of the bath will be hotter than others, causing more loss of acid from the tubes in the hotter location. In forty minutes all of the flakes of carbon are usually dissolved on a water bath. These baths are designed especially for this work, and contain racks to hold thirty-six tubes. These racks have false bottoms perforated with many small holes. This arrangement permits the tubes to be immersed to the depth of 28 mm., which is about the level of the nitric acid.

For more rapid solution of the carbon, requiring from four to seven minutes, use a sand or graphite bath heated to about 190° C. Plunge the tubes into the bath just to the top level of the acid in them. Keep the tubes close together and do not run more than six tubes at a time, as such a bath is liable to great variation in temperature. The writer collects a set of six tubes in a compact cluster and covers all with a 5-ounce beaker. This prevents too rapid loss of acid. Remove the tests the second that the brown flakes are in solution. Use standards within 5 "points" (0.05 per cent carbon) of the tests so that tests and standards will go into solution at about the same moment.

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* Quenching can be safely done provided the test piece is first cooled to a black heat in an entirely dark closet.

† Some laboratories use glass marbles that rest on the top of the test tubes during the boiling to reduce the evaporation of the acid.

The tests are quickly cooled in running water and compared in the bent-end comparison tubes, which permit the contents of the tubes to be mixed by a rocking motion. The comparison tubes are of 14 c.c. capacity, and graduated to tenths of a c.c. The length of the graduated portion is 181 mm. Then follows 45 mm. of ungraduated tube; then the part bent at an obtuse angle. The bent limb is about 50 mm. long. The outside diameter of the tube is 12 mm. A set of three of these tubes is used. The specifications for these tubes should require that all three tubes be the same inside and outside diameter throughout their graduated portion. The figures and graduation lines should be small, the figures not over 2 mm. long and the lines not over 4 mm. long for c.c., and not over 1½ mm. long for tenths of a cubic centimeter.

The graduations of all three tubes should coincide with each other. For example, the 14 c.c. mark should be exactly the same distance from the bottom of the comparison tube in each tube of a set, thus proving that the inside diameter is uniform throughout the set.

The tubes should be free of fine black lines due to bubbles in the glass when it was drawn into tubing.

The tubes should be made of selected tubing free of scratches. The graduations should be as exact as those of a burette.

All color carbons should be made in duplicate and results averaged. Nothing is gained by operating on a greater amount than 0.100 gram. The author, in his practice, ran a great many color tests, using 0.500 gram, and found the same lack of agreement, and much more acid needed.

The Comparison.—If, for example, a 0.60 carbon standard is in use pour it into the comparison tube, using as little rinse water as possible, so that the volume of the fluid in the tube is just 6 c.c.; mix thoroughly.

The test is then put in another tube, and water is added to it until its color is the same shade as that of the standard, mixing carefully with each addition of water. This matching should be conducted slowly when the test is still but slightly darker than the standard. But 0.2 cubic centimeter should be added at a time when the test is only slightly darker than the standard, so that when the former is finally very slightly lighter than the standard, the operator knows he has overstepped the end-point 0.01 per cent, which he deducts from the reading. If the test, for example, is just turned lighter at 6.5 c.c., then the per cent carbon will be 0.65 less 0.01 or 0.64 per cent carbon. If a standard of 0.30 carbon is in use, it is diluted to 9.0 c.c. Should the test match it at 6.0 c.c., then the carbon percentage will be 0.60÷3, or 0.20 per cent carbon. If a standard of 0.40 carbon is used, it is diluted to 8.0 c.c. If the test matches it at 7.0 c.c., for example, then the per cent carbon will be 0.70÷2, or 0.35 per cent carbon. If a standard of 0.08 per cent carbon is in use, it is diluted to 5.6 c.c. Should the test match it at 6.0 c.c., for example, the per cent carbon would be 0.60÷7, or 0.085= per cent carbon. When a large number of color tests must be made, they should be checked at frequent intervals by combustion; for instance, if a lot of thirty color tests are made, and every fifth one is checked by combustion and checks within 0.01 to 0.03 per cent in a range from 0.50 per cent and over, it is pretty safe to assume that that particular lot of color tests was done under favorable conditions.

The author does not use a comparison camera, but decidedly prefers to hold the tubes on a sheet of white paper, in diffused sunlight. The direct glare of the sun is, of course, undesirable.

At night a 50-candle power frosted electric lamp of filament type resting on a sheet of white paper from a flexible arm is the best source of light. The comparison tubes should be held * with the graduations touching each other, thus giving a clear field of color. Their relative right and left positions should be changed at intervals of a few seconds to assist the operator in judging respective depths of color. He should endeavor to lose track of which is test and which is standard, and if, under such conditions, he finds he can come to the same conclusion

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* The comparison tubes should be held at an angle of about 45° to the paper with their ends touching it.

three times in succession, then he is as certain as possible of his choice of the light one and the dark one. In the author's opinion the least source of error in carbon color work is the operator's eye. A man with a good eye for color and plenty of practice can be counted on not to introduce an error due to the eye of over 0.02 per cent in higher carbons and not over 0.010 per cent in lower carbons, around 0.08 and perhaps not over 0.005 per cent in the latter range.

Reject all drillings that are blued, or rusty.

CHAPTER XII

PART II

PHOSPHORUS IN PIG IRON, STEEL, WASHED METAL AND MUCK BAR *

DISSOLVE 1.63 grams of sample in 45 c.c. 1.13 nitric acid, using a 5-ounce beaker. Heat gently on hot plate or bath of some description. The author uses a twelve-hole affair as shown in Fig. 21. Highly silicious pig iron dissolves slowly and it is best to maintain all pig iron samples at digesting heat (barely boiling) for at least twenty minutes. To assist in dissolving pig iron add four drops of hydrofluoric acid to the solution after it has been digested ten minutes with the nitric acid, if high silicon is suspected.

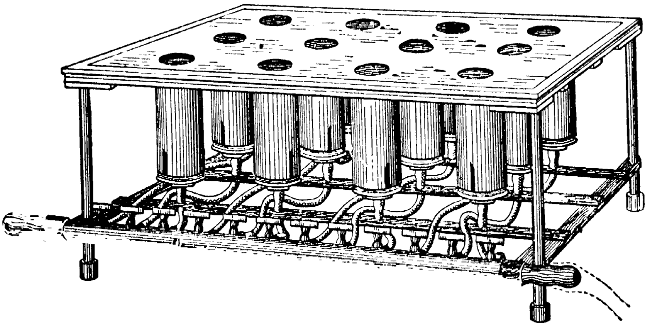

FIG. 21.

For pig iron and some chrome steels the next step is to filter out the insoluble graphite, etc. Wash the residue on the filter fifteen times with the dilute nitric acid wash. All phosphorus

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* Hundeshagen (modified by J. O. Handy) first recommended the titration of the yellow precipitate by standard alkali.

filtrations in this laboratory are made on a revolving filter stand. (See Fig. 22.)

It is not necessary to filter solutions in plain carbon steels. Filter the muck bar solutions if they contain much insoluble residue.

Add to the filtered solutions of pig iron, chrome steel and muck iron and to the unfiltered solutions of plain steel and

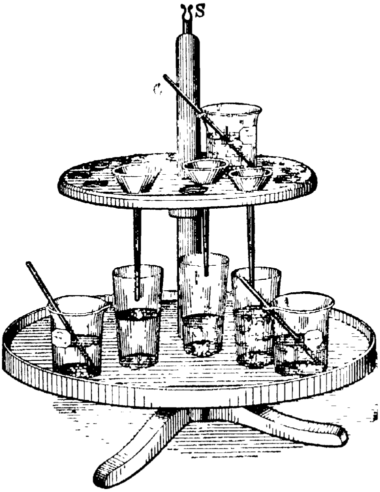

FIG. 22.

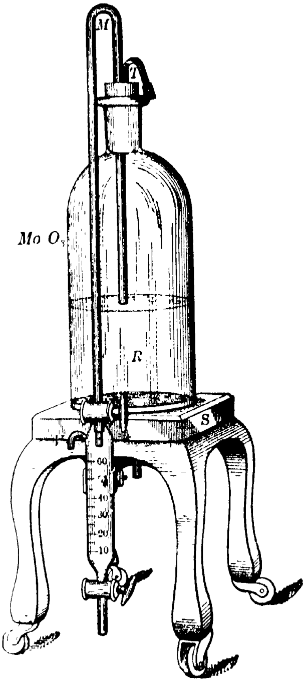

FIG. 23.

washed metal, from a convenient drop bottle, the potassium permanganate solution. Continue the addition of permanganate until the excess of manganese separates as a brown precipitate that does not disappear noticeably after ten minutes' boiling. As washed metal usually contains about 3.00 per cent of carbon it will consume considerably more of the permanganate solution before the carbon is destroyed than ordinary steel. The excess of manganese precipitate is removed by adding ferrous sulphate solution, free of phosphorus, from a dropper until the solution is again clear. After five minutes more boiling the beakers are removed from the fire, the covers are rinsed off and the inside walls of the beakers are washed (to prevent the phospho-molybdate sticking to the walls) down, and 50 c.c. of the ammonium-molybdate * are run into each test from a measuring siphon. (See Fig. 23.) A batch of twelve tests are stirred at a time, using glass rods. A single test is stirred around twice, then the next one, and so on until each test in the lot has been stirred ten times. This means that each solution has been stirred at intervals during a period of ten minutes. The twelve samples are put on the revolving stand and twelve 7 cm. filters are marked with a lead pencil to correspond to the respective tests. The only interval in plain Carbon Steel between the completion of the stirring and commencement of the filtration is the time required to fit the filter papers to the funnels.

The liquid is decanted through its proper filter and the bulk of the precipitate is allowed to remain in the beaker until the filter papers are washed ten times, giving each paper a washing, then the next one and so on until No. 1 is reached again. By the time No. 1 is ready for its second washing, the first washing will be well drained off. Each funnel stem is given a turn with the thumb and forefinger in such a manner that the double fold of the paper is washed twice and the single fold once during each washing. Use the dilute nitric acid wash.

Ten washings having been accomplished, the main body of the yellow precipitate is washed on to its respective filter with a fine jet of the acid wash, and receives a further ten washings to remove iron.

To remove free acid the precipitates are next washed thirty times with the potassium nitrate water. The filters are now removed to a large watch glass. A ruled slip is dated and headed and the various tests are entered thereon. On the right-hand side is kept a record of the alkali used, and on the left, the acid standard used in the subsequent titration of the yellow precipitate.

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* $H_3PO_4+12(NH_4)_2MoO_4+21HNO_3=(NH_4)_3PO_4\cdot 12MoO_3+21NH_4NO_3+12H_2O$.

The titration is accomplished by placing filter and precipitate in a 100 c.c. beaker. The standard sodium hydroxide solution, 1 c.c. of which equals 0.01 per cent phosphorus when 1.63 grams are taken, is dropped on the filter until the yellow precipitate has dissolved.* Then add 50 c.c. distilled water. Two drops of phenolphthalein are introduced, and from a second 50 c.c. burette standard nitric acid is run into the rose-colored solution until one drop of acid discharges this color. The total number of c.c. of alkali added, less the number of c.c. of acid required to discharge the rose color, multiplied by 0.01, gives the percentage of phosphorus in the sample.†

The following equation shows how the reaction proceeds:

$$2[(NH_4)_3PO_4 \cdot 12MoO_3]+46NaOH$$
$$=2(NH_4)_2HPO_4+(NH_4)_2MoO_4+23Na_2MoO_4+22H_2O.$$

According to the equation 1 c.c. of normal NaOH solution should equal 1.3494 mgs. of phosphorus (i.e., 40.008 grams NaOH dissolved in water and diluted to 1 liter = normal NaOH). $46NaOH = 2P = 62.08$ grams, or 46×40.008 grams $NaOH = 62.08$ grams of P, or 40.008 grams $NaOH = 1.3494$ grams P.

GRAVIMETRIC PHOSPHORUS

If it is desired to check the volumetric method by weighing the yellow precipitate, proceed exactly as given under the latter process, with the following exceptions:

First. Filter *all* solutions as in pig iron.

Second. Omit the washing with potassium nitrate and use only the dilute nitric wash to remove iron, leaving the acid in the filter paper.

Third. Filter the yellow precipitate on 7 cm. ashless filters that have been previously weighed hot between watch glasses with edges ground to fit water-tight when held firmly together, nearly full of water, in a vertical position.

These filters are weighed hot and as rapidly as possible after having been dried at the temperature of boiling water. The phospho-molybdate is collected on the weighed filters and washed free from iron with the dilute nitric acid. The filters are again dried as before, for one hour, and weighed. The weight of the filter paper plus the dried precipitate, less the weight of the paper, less the blank (obtained by filtering a clear filtrate from some previous phosphorus determination through a weighed paper, washing it, drying it and reweighing it as in an actual analysis) equals the percentage in the sample when 1.63 grams are used for analysis. This method is valuable only as a check, as too much time is consumed.

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* It is safer to add, at least, 1 or 2 c.c. excess of the alkali standard.

† Figs. 21, 22 and 23 were designed some years ago by Dr. Edward S. Johnson.

In both methods the filtrates and washings are placed on a shelf for one hour. If a cloudy ring forms at the junction of the washings and the main body of the filtrate, results will be too low. If the cloud gradually spreads, the results may be as much too low as 0.01 per cent in a possible 0.100 per cent.

After considerable practice one can estimate with sufficient accuracy for most mill control all phosphorus 0.02 per cent and under by simply examining the yellow precipitate after it has had an opportunity to settle for about twenty minutes in the 5-ounce beaker. The prevention of cloudy filtrates will be discussed under the heading "*Molybdate Solution.*"

Standard Sodium Hydroxide Solution.—One hundred and fifty grams of sodium hydroxide and 1 gram of barium hydroxide are dissolved in 1000 c.c. of water. Let the solution stand for two days. Siphon off the fluid and dilute it to 2 liters. Dilute 275 c.c. of this stock solution to 3500 c.c. Measure out exactly 100 c.c. for standardization, leaving 3400 c.c. On testing, suppose it is found that 20 c.c. of the alkali standard equal 20.75 c.c. of the acid standard. This gives the proportion 20 : 20.75 :: 3400 : $X(=3527)$. Therefore dilute the remaining 3400 c.c. to 3527 c.c. when 20 c.c. of the NaOH standard will equal 20 c.c. of the standard acid or 1 c.c. NaOH = 0.010 per cent phosphorus when 1.63 grams of sample are used for analysis. It is always best to confirm this value by running several steels whose phosphorus content is accurately known.

Standard Nitric Acid.—Dilute 74 c.c. 1.20 nitric acid to 3500 c.c. Draw off exactly 100 c.c. for testing. On titrating with standard NaOH, suppose it is found that 19.2 c.c. of the acid equal 20 c.c. of the alkali: 19.2 c.c. : 20 c.c. :: 3400 : X $(=3541)$.

Therefore the remaining 3400 c.c. are diluted to 3541 c.c. when 20 c.c. of standard acid should equal 20 c.c. of standard alkali.

For preparation of 1.20 specific gravity nitric acid from concentrated acid, see Chapter XX.

Acid Molybdate Solution.—Dissolve 183 grams of unignited molybdic acid plus 2 grams of ignited (melted) molybdic acid in 900 c.c. of 11.50 per cent ammonia water plus 250 c.c. of distilled water. Cool this solution and add it a little at a time to 2700 c.c. 1.20 nitric acid. Cool the nitric acid after each addition of the molybdate. If the nitric acid is allowed to get too greatly heated the molybdic salt will precipitate in large quantity. Filter through a pulp filter (using suction) after twelve hours' standing.

Some years ago the author observed that a solution of ammonium molybdate in nitric acid, made as here given, will produce different varieties of the yellow precipitate. Other conditions being unchanged, an ammonia solution of molybdic acid prepared from ignited, i. e., crystalline anhydrous molybdic acid, causes the yellow precipitate to separate from the nitric acid solution of the steel in an extremely fine state of division. Such a precipitate will remain suspended in the solution for hours without subsiding and will run through a filter paper almost as though it were a solution instead of a precipitate. This precipitate has only one redeeming feature: It is the least soluble in the dilute nitric wash of any of the varieties of ammonium phospho-molybdate that are encountered under the conditions that are cited here. Now if no ignited molybdic acid is used in the preparation of the molybdate solution, the phospho-molybdate settles rapidly and does not run through a filter. But this variety has the objection that it is the most soluble form of phospho-molybdate, in nitric acid. This variety of precipitate will leave the filtrate perfectly clear, but after the latter has stood for an hour (if much precipitate has dissolved in the wash water) or perhaps not until the next day (if little of the yellow precipitate has dissolved in the dilute nitric wash) a milky ring of phospho-molybdate will appear at about the point where the washings lie on top of the main body of the filtrate. If much of the yellow precipitate has been dissolved, say about $\frac{1}{10}$ or $\frac{1}{20}$ of its weight, this cloud will spread through the entire filtrate.

The ideal yellow precipitate is that one whose physical condition is such that it will give a clear filtrate and be practically insoluble in the wash. The author has had brands of molybdic acid that require equal weights of the crystalline molybdic acid and of the unignited variety to produce the desired results. At present but 2 grams of the crystalline material are needed for the particular brand of molybdic acid now in use.

To prepare crystalline molybdic acid the author melts in a porcelain dish the ammonia-free, so-called c.p., molybdic acid which melts rapidly at a bright red heat to a clear fluid, and, on cooling, forms handsome crystals that can be readily reduced to a powder in a porcelain mortar.

Potassium Permanganate Solution for Oxidation of the Carbon.—Fifty grams of the salt dissolved in 1 liter of water.

Ferrous Sulphate Solution.—Two hundred and fifty grams of the phosphorus-free salt dissolved in 1000 c.c. of water acidulated with 20 c.c. 1 : 3 sulphuric acid.

The Preparation of Ferrous Sulphate from Steel Drillings.—A very effective ferrous sulphate solution can be prepared as follows: Dissolve 55 grams of low phosphorus steel drillings in a mixture of 55 c.c. of conc. H_2SO_4 and 200 c.c. of water; add more water at intervals, heating gently. Do not boil. When all action is over dilute to 500 c.c.; filter through a large folded filter or on a plug of washed filter paper pulp; cool and dilute to 1000 c.c. with water.

Dilute Nitric Acid Wash.—Two hundred and thirty c.c. 1.20 nitric acid diluted with 8100 c.c. of water.

Potassium Nitrate Wash.—Dissolve 50 grams of potassium nitrate in 2500 c.c. of water for a stock solution.

Dilute 700 c.c. of the latter with 7000 c.c. of water to constitute the wash.

Phenolphthalein Indicator.—One gram of this substance is dissolved in 100 c.c. of absolute alcohol.

PHOSPHORUS IN VANADIUM STEEL

E. W. Hagmaier, in Met. Chem. Eng., Vol. XI, No. 1, separates the phosphorus by cerium chloride. In the case of a tungsten steel, dissolve the steel as for tungsten as given on pages 114 to 116. Instead of adding the molybdate solution as directed on page 116, this chloride solution should be entirely reduced with SO_2; then add 5 c.c. of 90 per cent acetic acid and 10 c.c. of a saturated solution of cerium chloride. Next add 1 : 3 ammonia slowly until a permanent turbidity is obtained. Boil; let settle; filter; wash a few times with hot water; dissolve in 1 : 1 hot nitric acid and precipitate the phosphorus with molybdate solution. If the vanadium is in excess of 1 per cent, the cerium phosphate must be redissolved, and reprecipitated to remove all of the vanadium. The cerium phosphate is then dissolved off the filter with the nitric acid and finished as above. See pages 318 to 323 for the author's method for phosphorus in the presence of vanadiam.

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* See remarks at the close of Chapter XI, page 269, on the proper way to drill a steel sample in order to obtain borings that represent the average of the piece in phosphorus, sulphur, silicon and carbon.

ACID MOLYBDATE SOLUTION NO LONGER USED

The author abandoned the use of the acid molybdate several years ago and uses the slightly ammoniacal water solution of ammonium molybdate instead. See page 323.

CHAPTER XII

PART III.

THE DETERMINATION OF PHOSPHORUS IN VANADIUM STEELS, FERRO-VANADIUM, NON-VANADIUM STEELS, AND PIG IRON, USING A FAINTLY AMMONIACAL WATER SOLUTION OF AMMONIUM MOLYBDATE.

I.—METHOD FOR STEEL CONTAINING VANADIUM UP TO 2.6 PER CENT

IBBOTSON and Brearley, in 1902,[†] recommended that phosphorus be precipitated from the *reduced* solution of vanadium, using ferrous sulphate as a reducing agent, claiming thereby to aid in the precipitation of phosphorus when vanadium is present.

Cain and Tucker, in 1913,[‡] recommended that the vanadium present be reduced with ferrous sulphate and sulphurous acid for the same purpose.

The method here[*] described gives a successful and convenient method for complete precipitation of phosphorus in the presence of highly oxidized vanadium:

Place 1.63 grams sample in 150 c.c. beaker. Dissolve in 45 c.c. HNO_3 (1.13 sp. gr.) over a low flame. When solution is clear and brown fumes have been driven off, add 3 c.c. $KMnO_4$ solution; boil three minutes; then add 3 c.c. $FeSO_4$ solution to dissolve precipitate due to the excess permanganate; boil until brown fumes are gone. Avoid large excess of ferrous sulphate.

Add 40 to 50 c.c. conc. HNO_3 (1.42 sp. gr.); bring to a boil; rinse cover and sides of beaker with least amount of distilled water; then add 50 c.c. of the water solution of ammonium molybdate. Stir vigorously for a minute or two and let stand overnight.

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[*] Reprinted from the Journal of Industrial and Engineering Chemistry, Vol. XI, No. 2, page 133. February, 1919.

[†] "Analysis of Steel Works Materials."

[‡] Jour. Ind. and Eng. Chem., V (1913), 647.

Decant through a 7 cm. paper, placing a little paper pulp in apex of filter, keeping the main precipitate in the beaker. Wash iron out of filter by washing fifteen times with the nitric wash, then proceed to pour the main precipitate on the filter.

Transfer all of precipitate as far as possible, with the aid of the nitric wash. Add about 2 c.c. of wash to the beaker and remove adhering particles with a rubber-tipped glass rod. Use a separate beaker for catching the washings. Wash fifteen times with the dilute nitric wash; then twenty-five times with KNO_3 wash, or until the outside of the filter has no sour taste, especially along the double thickness.

Place the filter containing the washed precipitate in a 150 c.c. beaker; add enough standard NaOH solution to cause the yellow color of the precipitate to disappear on macerating the paper to a pulp with a rubber-tipped stirring rod. Dilute to about 30 c.c. with distilled water; add a drop of phenolphthalein solution, which should cause a deep red coloration, otherwise more standard NaOH solution is needed; then titrate back carefully with standard HNO_3 solution until the pink just disappears. Subtract total c.c. of acid used from total c.c. of alkali used. The difference in c.c.×0.01 = percentage P.

TABLE I—SHOWING EFFECT OF INCREASING AMOUNTS OF NITRIC ACID (1.42 Sp. Gr.) ON PHOSPHORUS RECOVERY[1]

Vanadium Added Per Cent	15 c.c. HNO_3 Added P Found	30 c.c. HNO_3 Added P Found	40 c.c. HNO_3 Added P Found	50 c.c. HNO_3 Added P Found.
None	0.121	0.121 0.122	0.121 0.120	.... 0.121
0.20	0.119	0.121	0.121	.....
0.40	0.114	0.118	0.121	.....
0.60	0.111	0.117	0.120	.....
0.80	0.110	0.116	0.121	.....
1.00	0.110	0.115	0.120	0.119
1.40	0.110	0.112	0.121	0.122
1.80	0.105	0.112	0.119	0.121
2.20	0.099	0.111	0.119	0.120
2.60	0.093	0.108	0.117	0.117

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[1] This work was done with 1.63 grams samples of U. S. Bureau of Standards, 0.120 P standard, 10*b*.

Remarks.—The tests with the higher vanadium content were more tardy in precipitating than the lower ones, though all settled well after forty minutes' standing. Those to which 15 c.c. conc. HNO_3 were added gave deep orange precipitates, darkening in color about in proportion to the vanadium content, clinging tightly to the stirring rods and beakers. The three highest vanadiums are lower in yield of phosphorus than the preceding ones because of the impossibility of detaching the adhering precipitate from the stirring rods.

Those with 30 c.c. conc. HNO_3 were an improvement in speed of precipitation, color of precipitate, and cleaning from beakers and rods. Those with 40 c.c. and 50 c.c. showed the best colored precipitates, i.e., nearest the normal yellow phosphomolybdate color and gave water-white washings, from which no recoveries of phosphorus were made. The 50 c.c. ones were a little prompter than the 40 c.c., though both sets were a vast improvement over the 15 c.c. and 30 c.c., and both cleaned very easily from beakers and rods and gave good results.

The precipitate from the 15 c.c. conc. HNO_3 in particular seemed to be too finely divided and passed through the pores of the filter, necessitating reprecipitation of the washings in all those of higher vanadium content.

The vanadium was added as nitrate from an acid solution made as follows: Fuse 4.5 grams V_2O_5 (56.14 per cent V) with 10 grams Na_2CO_3 in a platinum crucible for ten to fifteen minutes. Let cool; place in a 400 c.c. beaker; add 10 c.c. water; then HNO_3 (1.20 sp. gr.) until effervescence ceases and 25 c.c. in excess. Rinse off crucible thoroughly with distilled water; cool solution to room temperature; transfer to 500 c.c. flask; dilute to the mark with water; stopper, and shake to mix thoroughly. 1 c.c. = 0.00505 gram. V. 1 per cent V in 1.63 grams sample = 3.25 c.c. solution.

The vanadium was added after the tests were weighed and before the 45 c.c. HNO_3 (1.13 sp. gr.) were added. The vanadium was, in each instance, reduced from yellow to green, due to the action of the reducing gases liberated by the reaction between the acid and the steel. The 40 to 50 c.c. conc. nitric added just before removing from the fire caused the yellow vanadic color to return.

Solutions Required.—*Nitric Acid for Titrating.*—Dilute 35.4 c.c. HNO_3 (1.42 sp. gr.) to 4000 c.c. with distilled water.

Stock Solution of Sodium Hydroxide.—Dissolve 150 grams NaOH (c.p. sticks) and 1 gram $Ba(OH)_2$ in 1000 c.c. water. Stir well and allow to stand twenty-four hours. Filter off the clear solution (or decant if preferable) and dilute with an equal volume of distilled water. Put into a 2-liter bottle and close with a rubber stopper.

Sodium Hydroxide Solution for Titrating.—Dilute 566 c.c. stock solution to 8000 c.c. with distilled water.

Ferrous Sulphate Solution.—Dissolve 55 grams steel (low in phosphorus and sulphur) in 1000 c.c. beaker in 720 c.c. H_2SO_4 (1 : 3). Add a little water occasionally to prevent salting out, and heat gently, but do not boil. Filter, cool, and dilute to 1000 c.c.

Potassium Permanganate Solution.—Dissolve 50 grams $KMnO_4$ in 1000 c.c. water.

Nitrate Wash.—Dissolve 8 grams KNO_3 in 8000 c.c. water.

Acid Wash.—Dilute 102.4 c.c. HNO_3 (1.42 sp. gr.) to 8000 c.c. with water.

Faintly Ammoniacal Water Solution of Ammonium Molybdate.—Into each of four 800 c.c. casseroles weigh 55 grams ammonium molybdate and 50 grams ammonium nitrate, and add 40 c.c. ammonium hydroxide (0.95 sp. gr.). Dilute each to 700 c.c. with water. Heat for about thirty minutes, stirring once in a while until all salts are in solution. Combine contents of the four beakers by pouring into a large bottle; then dilute to 4000 c.c. with water. Let stand overnight. Filter the insoluble material through double 15 cm. papers. *Do not wash.* The clear solution thus obtained should remain clear indefinitely. Do not filter out the insoluble material until the total mixture from the four beakers has stood overnight. The insoluble should not weigh over 1 or 2 grams.

II.—METHOD FOR PHOSPHORUS IN U. S. STANDARD STEELS AND PIG IRONS TO WHICH HAVE BEEN ADDED 28 PER CENT VANADIUM AND IN FERRO-VANADIUM CONTAINING 56.7 PER CENT VANADIUM

Procedure.—Weigh out 0.5 gram steel and 0.5 gram V_2O_5 (56.14 per cent V). Transfer to 250 c.c. porcelain dish. Digest with a mixture of 30 c.c. HCl (1.20 sp. gr.) and 30 c.c. HNO_3 (1.42 sp. gr.) for about one hour; then rinse off cover, add 100 c.c. HNO_3 (1.42 sp. gr.), and take to dryness. Bake five minutes at 750° C. in an electric muffle furnace.

Dissolve the oxides in 35 c.c. conc. HCl, evaporate to 10 c.c.; add 50 c.c. HNO_3 (1.42 sp. gr.), take to 10 c.c. volume, then add 10 c.c. more strong nitric and heat awhile with cover glass on. Filter through a platinum Gooch crucible with a thin pad of acid-washed asbestos, using suction. Wash fifteen times, using the following wash: 200 c.c. HNO_3 (1.42 sp. gr.), 100 c.c. water, and 20 grams $Fe(NO_3)_3$. (Ferric nitrate made by dissolving 5 grams low phosphorus, melting bar steel in 50 c.c. HCl (1 : 1) and taking to syrupiness twice with 50 c.c. HNO_3 (1.42 sp. gr.) each time.)

Concentrate the filtrate from the separated V_2O_5 to 10 c.c. in 150 c.c. beaker and filter out the second crop of vanadium "rust" as before. A third concentration to 10 c.c. should show no "rust" (V_2O_5).

To the third concentration add 40 c.c. HNO_3 (1.42 sp. gr.), and bring to a boil; rinse cover and sides with water and precipitate with 50 c.c. of the faintly ammoniacal ammonium molybdate solution. Stir vigorously for about two minutes. Let stand one hour; filter and wash as described for steels containing up to 2.6 per cent V. Titrate with alkali and acid in the usual manner.

TABLE II—RESULTS OBTAINED USING THIS METHOD ON U. S. STANDARDS

No.	Standard.	V_2O_5 Added Mg	P Found Per Cent	Per Cent P Given by U S Govt.
1	Iron D, *6a* V_2O_5......	500	0.522	0.526
2	Iron D, *6b* V_2O_5......	500	0.531	0.531
3	*10b* V_2O_5	500	0.124	0.120
4	*10b* V_2O_5.............	600	0.115	0.120
5	No. 20 Standard V_2O_5.	500	0.033	0.031
6	No. 20 Standard V_2O_5..	600	0.033	0.031

In the above procedure an average of 0.007 per cent P was found in the V_2O_5 added.

TABLE III—PHOSPHORUS IN FERRO-VANADIUM, 56.7 PER CENT VANADIUM

Author's Method by Removal of about Two-thirds of V_2O_5 and Pptn with Faintly Ammoniacal Ammonium Molybdate Solution	V_2O_5 Reduced with $FeSO_4$ and H_2SO_3 Pptn with Acid Molybdate Solution No V Removed	Acid Molybdate Pptn No Extra HNO_3 Added No V Removed	Faintly Ammoniacal Ammonium Molybdate Pptn. plus 40 c.c. HNO_3 (1.42 sp. gr.) No V Removed.
Per Cent P.	Per Cent P	Per Cent P	Per Cent P.
0.414	0.240	0.053	0.185
0.418	0.232	0.108	0.183
0.397	0.235		. . .
0.401	0.228		. . . .
. . .	0.234		. .
. . .	0.260		. .
.	0.220		

III.—METHOD FOR DETERMINING PHOSPHORUS IN NON-VANADIUM STEELS AND PIG IRON, USING A FAINTLY AMMONIACAL WATER SOLUTION OF AMMONIUM MOLYDBATE.

Procedure.—Weigh 1.63 grams sample into 150 c.c. beaker. Dissolve in 45 c.c. HNO_3 (1.13 sp. gr.) over low flame. (In case ot pig iron and certain chrome steels, when all metal is in solution filter off carbon residue through 7 cm. paper; wash fifteen times with dilute HNO_3, wash, catching filtrate in 150 c.c. beaker. Concentrate filtrate to original volume.)

Add about 3 c.c. of the $KMnO_4$ solution, boiling for three minutes, then just enough $FeSO_4$ solution (about 3 c.c.) to dissolve the oxides of manganese. Boil off brown fumes. Add 15 c.c. HNO_3 (1.42 sp. gr.). Rinse cover and sides of beaker with least amount of water, add 50 c.c. ammonium molybdate solution, and stir briskly until phosphorus precipitate is completely formed (about two minutes' stirring). Let stand one-half hour or less. Filter through 7 cm. paper; wash fifteen times with dilute HNO_3 wash; then with nitrate wash until the outside fold of the filter has no sour taste. In case of high phosphorus samples this may mean as much as thirty-five or forty times.

(The washings in such a case were kept separate from the main filtrate, concentrated to 10 c.c., acidified with 15 c.c. conc. HNO_3 and 50 c.c. of ammonium molybdate solution added.

It was then allowed to stand overnight. There were no recoveries, showing the insolubility of the precipitate in the wash.)

TABLE IV—COMPARING RESULTS OBTAINED WHEN USING FAINTLY AMMONIACAL WATER SOLUTION WITH THOSE OBTAINED BY USE OF A NITRIC ACID SOLUTION OF AMMONIUM MOLYBDATE[1]

Sample No	Slightly Ammoniacal Water Solution of Molybdate Per Cent P Found	Nitric Acid Solution of Ammonium Molybdate Per Cent P Found
9	0.054	0.056
34	0.023	0.023
7132	0.019	0.018
3622	0.056	0.054
1	0.013	0.014
2	0.058	0.058
4	0.042	0.044
5	0.052	0.052
70 055	0.055	0.052
80 042	0.042	0.044
x, pig	0.736	0.730
r, steel	0.006	0.004
3641	0.050	0.049
34	0.025	0.025
39	0.058	0.056
Pig iron standard, A	0.097	0.096

[1] See *Iron Age*, April 5, 1917

TABLE V—SHOWING RESULTS OF TESTS ON U. S. GOVT. STANDARDS

Sample.	P Found Per Cent.	U S Bureau, P Value Per Cent
Pig iron, D, third set	0.610	0.602
Pig iron, B 6*a*	0.104	0.105
Pig iron, D 6*a*	0.540	0.545
Steel, 10*b*	0.119	0.120

This method is the same as the one published by the author in *Iron Age*, April 5, 1917, except that it was afterwards found that more rapid precipitation of the yellow precipitate was secured by the addition of 15 c.c. of concentrated nitric acid (or 30 c.c. 1 : 1 acid is safer to handle) to the boiling solution of the sample just before removing from the fire to add the molybdate solution; and 1.13 sp. gr. HNO_3 is used instead of 1.20 as the steels in general dissolve more rapidly in the 1.13 acid.

Advantages of the Foregoing Methods for Ordinary Routine Work on Plain and Other Steels.—(1) The simplicity of the preparation of the faintly ammoniacal water solution of ammonium molybdate as compared with the elaborate method of preparing the old acid molybdate solution in nitric acid.

(2) The handling of the acid molybdate is disagreeable, hard on the clothing and fingers of the operator and on table tops. The slightly ammoniacal water solution is harmless in these particulars.

(3) As stated, the slightly ammoniacal water solution keeps as clear as distilled water after it has been properly filtered; and its precipitating power is constant, whereas the old acid solution soon becomes turbid and therefore its precipitating power is continuously lessened.

(4) The interference of vanadium up to at least 2.6 per cent V in the determination of phosphorus is prevented in a simple way and the true phosphorus is obtained from ferro-vanadium containing the very high vanadium content of 56.7 per cent.

Acknowledgment.—Credit is due Mr. F. D. Hawkins for his careful analytical work when making the trial analyses required by the author to prove the foregoing.

CHAPTER XII

PART IV

THE ANALYSIS OF FERRO-PHOSPHORUS

SILICON

FUSE 0.5 or 0.6 gram of the floured sample in a finely ground mixture of 10 grams of sodium carbonate and 2 grams of potassium nitrate in a platinum crucible. After a complete fusion is gotten as shown by the melt being practically free of boiling at a bright red heat, cool the melt by running it around the sides of the crucible; dissolve it out of the crucible with water in a platinum dish; transfer the water solution and all to a 600 c.c. casserole, cleaning the crucible by heating in it some conc. HCl; add the cleanings to the casserole whose contents have been meanwhile acidulated with 75 c.c. of conc. HCl. Heat the casserole with a watch glass on it until all effervescence has ceased; remove the cover and evaporate to dryness; cool; add 20 c.c. of conc. HCl; heat for some minutes to dissolve the iron; add 150 c.c. of water and heat again to dissolve the sodium salts; filter out the silicic acid and wash it free of iron test with 1 : 20 HCl. Burn off the paper containing the silicious matter in a weighed platinum crucible and finish it as in steels, using HF and a few drops of H_2SO_4. (See page 349.) The residue remaining after volatilizing the silicon may contain a little iron and phosphorus. Fuse this residue with twenty times its weight of anhydrous sodium carbonate; dissolve the fusion with HCl and add the solution to the main filtrate from the silicious matter.

PHOSPHORUS

The main filtrate from the silicon now contains all of the phosphorus and iron. Dilute this filtrate to 400 c.c. with water;

add 2 grams of citric acid, to keep the iron from reprecipitating, and then a slight excess of ammonia. Heat the solution to nearly boiling and pass through it a stream of hydrogen sulphide that has been washed by bubbling through a wash bottle containing about an inch of distilled water. The original form of the 2 quart Kipp is the most practical form of H_2S generator. The iron sulphide that is supplied fused and in sticks is the best for this work. The 1 : 1 HCl should be used to attack the iron sulphide. When the black sulphide in the main filtrate has settled out well and falls to the bottom of the beaker, stop the stream of the H_2S and filter out the sulphides of iron and some platinum (the crucible is attacked some by the niter in the flux). Wash the sulphides about fifteen times with water saturated with H_2S. Place the filter containing the sulphides in a porcelain dish and pour over it 30 c.c. of 1 : 1 HCl and warm it with the cover on at not over a water-bath temperature for an hour to dissolve the iron sulphides. If platinum is present there will remain some insoluble platinum sulphide which can be filtered out together with the paper pulp from the first filter which was placed on the acid. The second filter is washed at least twenty times with 1 : 40 HCl and then further until the washings no longer give an iron test with either potassium ferricyanide or with ammonium sulphocyanate. This filtrate and washings from the pulp and platinum sulphide contain all of the iron and perhaps still a portion of the phosphorus. Two grams of citric acid are again added and the iron is again separated in hot solution with H_2S as before. Filter out the sulphide of iron and wash it as in the first instance. Retain the iron sulphide to get the total iron. The two sets of filtrates and washings from the H_2S precipitations are combined and made acid with about 50 c.c. of 1 : 1 HCl and are heated with a cover on until all effervescence due to the escape of H_2S is over. Remove the cover and evaporate to 100 c.c.; add water if necessary to dissolve any crystals that may have formed; filter out any insoluble matter; add 150 c.c. of conc. nitric acid and heat in the covered beaker until all action between the nitric acid, the chlorides, and the citric acid is over; then transfer to a large casserole and evaporate low. When brown fumes begin to develop again, cover the vessel and add 50 c.c. more of the conc. HNO_3. Heat until all action is over; remove the cover and evaporate to dryness;

cool; add 75 c.c. of conc. HCl; cover; heat until action ceases; evaporate again to dryness; cover again; add once more 75 c.c. of HCl and evaporate dry; cool; heat with 25 c.c. of conc. HCl with the cover on for ten minutes; add 150 c.c. of water to dissolve the salts; filter; wash the filter with water until the washings are free of chlorides; make the filtrate and washings just neutral with ammonia; cool; add 40 c.c. of magnesia mixture; stir well; add to the solution one-third of its volume of conc ammonia; and stir the solution for one or two minutes and let it stand for twelve hours. Then filter out the ammonium magnesium phosphate and wash it with 5 c.c. of conc. ammonia diluted with 500 c.c. of water, until the washings no longer give a cloudiness after being acidulated with a few drops of dilute nitric acid and tested with a little silver nitrate solution. The washings should be kept separate from the main filtrate. Both the filtrate and washings should be tested by adding 10 c.c. more of the magnesia mixture and to the washings should be also added one-third of its volume of ammonia. If any precipitate forms in either the filtrate or the washings it is filtered, washed and added to the main precipitate. Dry the filters containing the phosphate precipitates, and then smoke off the volatile portion of the filter papers below redness to avoid losing particles of the phosphate; do not heat the platinum crucible hot enough to ignite the gases coming from the papers. When the smoking ceases, raise the heat to low redness, and finally hot enough to obtain a pure white residue of magnesium pyrophosphate. Do not use a blast lamp temperature as the platinum will be badly attacked by the phosphate. Weigh the $Mg_2P_2O_7$; dissolve it in HCl; filter out any insoluble silica; wash it; weigh it and deduct it from the first weight; calculate the net weight to metallic phosphorus by use of the factor 0.2787.

Magnesia Mixture consists of 25 grams of magnesium chloride, 50 grams of ammonium chloride, 100 c.c. conc. ammonia and 200 c.c. of water. This mixture is stirred until the salts are dissolved, and after standing for at least twenty-four hours it is filtered for use.

Sulphur in ferro-phosphorus is obtained by fusing the finely ground sample as given for phosphorus, continuing the analysis exactly as for this element until the silicon has been filtered off. The filtrate and washings from the silicious matter are then diluted to 400 c.c. and the sulphur is precipitated with $BaCl_2$, using 25 c.c. of a saturated solution of the barium salt. The barium sulphate is filtered off after twelve hours and the determination is then finished as in steels.

Iron is obtained from the sulphide gotten from the second precipitation with H_2S in the analysis for phosphorus. The sulphide is roasted in a porcelain crucible until free of the paper; the ash is dissolved in HCl; reduced with stannous chloride and titrated with potassium dichromate as in iron ore. The iron can also be obtained in the sulphur determination by fusing 1 gram of the sample as above for sulphur; the filtrate from the silicious matter can be divided into two equal parts and one part can be finished for sulphur and the other half is precipitated with ammonia to remove the platinum from the iron. The latter is then dissolved off the filter with HCl and finished as given for iron ore. Sulphur can also be gotten by carbonate and peroxide fusion in an iron crucible as on pages 47 and 57.

Manganese is gotten in the same manner as for manganese in insoluble ferro-titanium. (See page 48.)

TYPICAL ANALYSES

	No 1	No 2
Iron	79 44	78 16
Manganese	0 05	0 06
Phosphorus	18 51	20 45
Sulphur	0 67	0 55
Silicon	0 76	0.54
Carbon	0.26	0.16

CHAPTER XII

PART V

SULPHUR IN STEEL, MUCK BAR, PIG IRON AND WASHED METAL

VOLUMETRIC

DISSOLVE 3 grams of sample in 70 c.c. of 1 : 1 * hydrochloric acid. More than this amount of acid is sometimes required for rapid solution. The dissolving flask is the author's design and is made in a mold with a *fire finish*, ring neck. The flask, being made in a mold instead of by hand, has a perfectly round neck and always takes a No. 6 rubber stopper. Its capacity is 275 c.c. to base of neck, and its height is 165 mm. It is a great convenience to have these details always the same. (Fig. 23A.) Previous to designing this flask much trouble was experienced in different lots of flasks. In the same lot some would require a No. 4, others a No. 5, and some a No. 6 stopper to get a good fit. Then ground finish flasks will crack at the neck when placed in the heater to dry out the water. Drillings are never weighed into wet flasks. The No. 6 stopper is perforated with three holes, one to receive a bulb funnel of 75 c.c. capacity. This funnel is also designed to facilitate the work. It has an opening at the top of the bulb of 15 mm. diameter. The glass cock has an extra large hole bored in it (3½ mm. diameter) to permit of rapid flow of the acid from the bulb into the flask. The total distance from the base of the bulb to the outlet in the stem is 145 mm. The second hole in the stopper admits

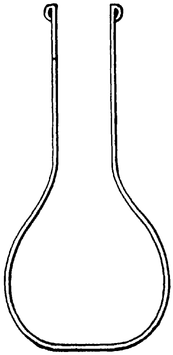

FIG. 23A.

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* Two parts of 1.20 HCl (conc.) to 1 part of water are more reliable as some kinds of pig iron show no sulphur at all by the evolution method with weaker acid.

a small tube that dips just below the level of the fluid in flask. After the iron is completely dissolved, hydrogen is forced through this inlet for from three to five minutes to drive out any hydrogen sulphide that may remain in the interior of the flask. The third hole admits the delivery tube which carries the evolved gases to the bottom of the absorbing solution of ammoniacal cadmium chloride. This solution is contained in a thick-wall, thick-bottom, test tube about 10 inches by 1 inch. Fifty c.c. of the solution are used for each analysis.

THE EVOLUTION APPARATUS FOR THE DETERMINATION OF SULPHUR IN PLAIN CARBON STEELS.

The bulb funnel referred to on page 330 is shown at *H* in Fig. 24. At *D* the thick wall, 10×1 inch, containing the ammoniacal cadmium chloride solution is given. The tube *F* with its four branches distributes the hydrogen to each dissolving flask *E*. On each branch a screw pinch cock, not shown in the cut, is located at the point *G* to shut off the hydrogen from any one flask *E*. The delivery tubes are as shown at *C*.

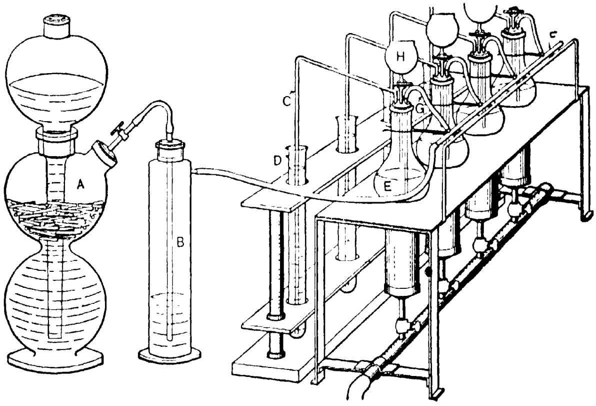

FIG. 24.

The flask is clamped in a rack supporting four flasks to the stand.* Each stand is supplied with four burners. The top of the stand on which the bottoms of the flasks rest is an asbestos copper-rimmed board with a circular hole of 42 mm. diameter cut in it immediately over each burner. The bottom of the flask rests in this hole. Ranged alongside of this rack is a wooden one holding the four absorption tubes. As many such sets of four are in operation at one time as the chemist can manage

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* See Fig. 24.

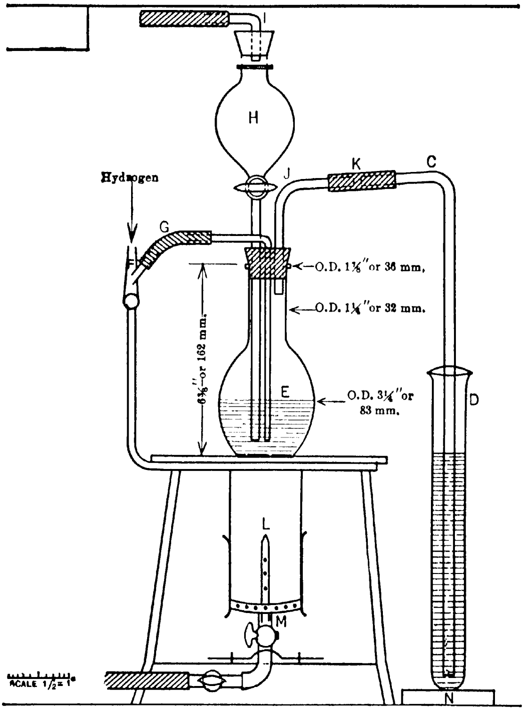

FIG. 25.

When the solutions no longer evolve gas to any extent without the aid of heat, the flames are raised slightly so as to maintain

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[*] Drawing No. 25 shows the connections for a single flask for the evolution of sulphur in steel, etc. This arrangement differs from that shown on page 331 in that the delivery tube is disconnected at *K* when the evolution is completed. The tube *J* is left permanently in the stopper. This is a much safer arrangement than the old one where *J* and *K* and *C* were all one piece of glass tubing. By the old way frequent breakages resulted at *J* and quite a few cut fingers.

a very slight boiling action. When heat no longer produces gas bubbles in the absorption tubes, the hydrogen is turned in and a rather rapid passage of this gas is continued for from three to five minutes. The cocks on all of the bulb funnels are then opened. The hydrogen is shut off at each flask.

The cadmium solution containing the precipitate of sulphide is poured on a rapid running 11 cm. filter. The absorption tube is rinsed with water and the washings are poured on the filter. The latter is washed three or four times with water. The delivery tube, if much precipitate adheres to it, is cleansed by rubbing it with a little filter paper. This small piece of paper is then dropped in on the main portion of the cadmium sulphide to which it belongs. The delivery tube, without further washing, is put back into its respective absorption tube.

Both tubes together with the filter paper containing the major part of the sulphide are taken to the titration table together with the other tests which have been similarly perpared. The filter paper with the adhering sulphide is placed in a 1000 c.c. beaker containing 500 c.c. of water. For convenience the beaker should have an etched mark on it to indicate the half liter.

The paper is beaten into fragments with a glass rod and the pulp is stirred all through the water. Two c.c. of starch solution are added. The absorption tube corresponding to this filter is filled one-quarter full of distilled water and then to within an inch of the top with 1 : 1 hydrochloric acid. Further, the delivery tube, which has been momentarily removed from the absorption tube previous to adding the water, is returned to the acid fluid, and is raised and lowered in it to dissolve any small quantity of cadmium sulphide adhering to its interior or exterior walls. It is then laid aside and the fluid in the absorption tube is poured into the water containing the bulk of the yellow sulphide. This acid is not dumped in promiscuously but is allowed to run down the inner wall of the beaker rather slowly so as not to disturb the contents thereof. Before stirring the acid through the latter, iodine is dropped in from a Gay-Lussac burette held in the operator's left hand. The drops are added in such a way that a circle of drops extends around the inner circumference of the beaker. With his other hand the operator now gives the solution in the beaker a *slight* stir with a glass rod. If this causes the blue to disappear, leaving a reddish tint, another circle of drops of iodine is added, and so on until two or three drops of the standard iodine solution produce a purplish blue end-point which does not fade to a red with more stirring.

The number of c.c. of iodine used less the number of c.c. required to produce a faint blue in a blank test, multiplied by the percentage value in sulphur of the iodine standard, equals the per cent of sulphur. The blank test is made on the same amounts of starch, filter paper and water as are used in an actual analysis.

This sulphur value is obtained by running steels of known sulphur content in the manner described.

The U. S. Bureau of Standards, Washington, D. C., also furnishes phosphorus, sulphur, silicon, and manganese standards for pig iron and steel that have been analyzed by chemists experienced in iron and steel analysis. These constitute a valuable aid to the analyst, enabling him at any time to check his own standards. The cost of these standards is low. Steps are being taken with a view to preparing also a series of various alloy steel standards standardized as to vanadium, titanium, chromium, tungsten, and molybdenum content.

Each day a standard steel should be run with the other work, as new acids and chemicals are liable to cause the sulphur value of the iodine to change from that originally obtained when it was first standardized.

This method is accurate for all unhardened plain carbon steels, and for annealed pig iron and for muck bar. In chilled pig iron, unless first annealed, the results are usually about 25 per cent lower than the actual sulphur, and yet, in spite of this fact, by reason of its rapidity, practically the method as given is very generally in use by buyer and seller of pig iron. The practice of annealing the drillings in covered crucibles, at a red heat, for fifteen minutes may probably come into vogue.

However, if the buyer and seller understand the limitations of the method it would seem unnecessary to resort to this detail. The steel furnace superintendent could calculate his sulphur

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[*] As is generally known, the U. S. Bureau of Standards now has plain vanadium, chrome-vanadium, chrome-nickel, chrome-tungsten and plain nickel standards for distribution at a reasonable rate.

content one-fourth higher than the laboratory report. Or the buyer and the seller could agree that if their respective laboratories find 0.060 per cent sulphur, for example, in pig iron, it shall be reported as 0.075 per cent, thus saving valuable time in the laboratory and yet have records that are sufficiently close to the truth for all practical purposes.

The evolution method is unreliable for steels high in copper and for many alloy steels that form carbides that are insoluble in 1 : 1 hydrochloric acid. The results are too low. (See pages 122–128.)

The Starch Solution.—Grind 1 gram of good wheat starch, free from rancid smell, to a powder. Stir it with 10 c.c. of water in a small beaker and pour it carefully into 90 c.c. of boiling water. Cool and use as needed. It is best to prepare this solution daily.

Iodine Standard.*—One gram of best resublimed iodine is dissolved in a very little water together with 10 grams of c.p. potassium iodide. This is diluted to 1000 c.c. with distilled water. It is standardized against a steel of known sulphur content.

Cadmium Chloride Solution.—Twenty grams of anhydrous cadmium chloride are dissolved in 1400 c.c. of ammonia water of 0.9 specific gravity. This solution is diluted to 4 liters with distilled water for use.

Lead Acetate Solution.—For purification of the hydrogen before it enters the sulphur flasks, it is allowed to bubble through a 500 c.c. Bunsen wash bottle containing a solution of lead acetate made as follows: (1) Dissolve 100 grams of lead acetate in 400 c.c. of water. (2) Dissolve 400 grams of potassium hydroxide in 500 c.c. of water. Pour one solution into the other and mix thoroughly. Use 120 c.c. of this solution in each wash bottle.

The hydrogen is generated in an ordinary Kipp apparatus.†

GRAVIMETRIC SULPHUR IN PIG IRON, STEEL, WASHED METAL AND MUCK BAR

Dissolve 5 grams of drillings of 0.04 per cent and higher sulphur content in 200 c.c. concentrated nitric acid, using an

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* One c.c. of this standard equals from about 0.0042 to 0.0045 per cent of sulphur when 3 grams of sample are taken for analysis.

† See pages 331 and 525.

800 c.c. beaker. For percentages of sulphur under 0.04 per cent use 10 grams of drillings, dissolving the latter in 300 c.c. of concentrated nitric acid. Add the nitric acid a few c.c. at a time, as the reaction is violent. When all acid is in the beaker, warm the contents of same until action is over. Then add 2 grams of sodium carbonate. Transfer the solution to a No. 6 dish and evaporate on the sand or graphite bath to dryness. Dis-

PHOTO NO. 26.

content one-fourth higher than the laboratory report. Or the buyer and the seller could agree that if their respective laboratories find 0.060 per cent sulphur, for example, in pig iron, it shall be reported as 0.075 per cent, thus saving valuable time in the laboratory and yet have records that are sufficiently close to the truth for all practical purposes.

The evolution method is unreliable for steels high in copper and for many alloy steels that form carbides that are insoluble in 1 : 1 hydrochloric acid. The results are too low. (See pages 122–128.)

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The hydrogen is generated in an ordinary Kipp apparatus.†

GRAVIMETRIC SULPHUR IN PIG IRON, STEEL, WASHED METAL AND MUCK BAR

Dissolve 5 grams of drillings of 0.04 per cent and higher sulphur content in 200 c.c. concentrated nitric acid, using an

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* One c.c. of this standard equals from about 0.0042 to 0.0045 per cent of sulphur when 3 grams of sample are taken for analysis.

† See pages 331 and 525.

CHAPTER XII

PART VI

MANGANESE IN PIG IRON, TUNGSTEN STEEL, MUCK BAR, NICKEL STEEL, MOLYBDENUM STEEL, VANADIUM STEEL, TITANIUM STEEL AND CHROME STEEL

FOR pig iron, muck iron, plain carbon, or plain vanadium steel or nickel steel, titanium steel with *absence* of chromium and with silicon not over 3 or 4 per cent, and tungsten steel not much over 3.5 per cent tungsten, accurate to 2 per cent of manganese. Dissolve 0.100 gram for manganese of not over 1 per cent manganese or 0.050 gram for higher percentages in 40 c.c. 1.20 nitric acid in a 10 by 1 inch test tube over a low Bunsen flame. (See Fig. 27.)

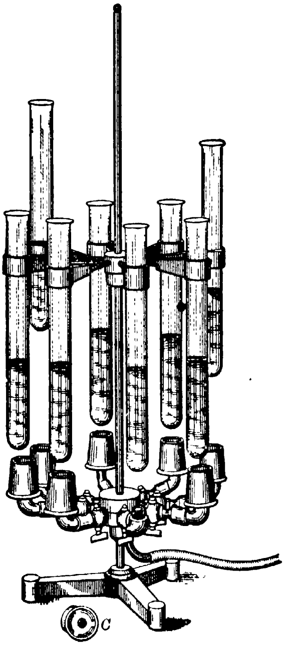

FIG. 27.

Boil until red fumes are gone. Revolve the tubes from over the flame and add cautiously 1 gram of light-brown colored peroxide of lead free from manganese. Do not use lead peroxide of the very dark brown, in some instances, almost black color as this very dense variety does not yield its oxygen readily, and results will not check and are frequently 25 per cent too low. Insist on getting light-brown lead peroxide.

Fig. 27 is after a design by Dr. E. S. Johnson.

After adding the lead to all of the tubes, raise the flames causing the contents to boil almost to the top of the test tubes, four minutes. Lower the flames, place the tubes *quickly* in cool water, and then, after a few seconds' delay, directly into cold water. Permit the excess of lead peroxide to settle ten minutes, or longer if convenient, in a dark cupboard.

Decant the contents of the tubes into 5-ounce beakers as needed, leaving all black sediment in the bottom of the test tube. Titrate the pink solution with standard sodium arsenite until all pink or brown shades are gone and a suggestion of yellow color appears. The author has tried many methods for the quick determination of manganese, and can recommend it in preference to other methods for simplicity, speed, and accuracy. Chromium is about the only disturbing element likely to be met with in steels, and can be quickly removed by the following method, which is used also for all high-speed combinations and high per cent tungsten steels.

Dissolve 0.300 gram or 0.150 gram in low and high manganese steels, respectively, and proceed exactly as given for the determination of manganese in chrome-vanadium steels. (See Analysis of Vanadium Steels, pages 32–33.)

For plain molybdenum steels without chromium, proceed as in plain steels. Presence of large quantities of copper and nickel do not interfere with this method. Of course, hydrochloric acid should be absent, or any other substance that would reduce permanganic acid, such as carbonaceous materials. Sunlight bleaches the pink color, causing low results.*

Standard Sodium Arsenite Solution.†—*Concentrated Stock Solution.*—2.48 grams of c.p. arsenious acid and 12.5 grams of c.p. fused sodium carbonate dissolved in 1250 c.c. of distilled water. Dissolve the arsenious acid and the carbonate, at first, in a little hot water.

Working Strength.—200 c.c. of stock solution diluted with 1600 c.c. of water. One c.c. of this solution will equal, usually, 0.07 per cent of manganese when 0.100 gram of sample is taken. It should be checked against steels of known manganese content before it is used.

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* For determination of manganese in cobalt steels, see page 389.

† Deshay suggested the sodium arsenite titration.

RAPID METHOD FOR PRELIMINARY BATH TESTS. TIME, TEN MINUTES FOR ALL OPERATIONS; FIFTEEN MINUTES ENOUGH FOR TEST IN DUPLICATE

Use a cone flask with a lip measuring 1¼ inches top, 2¼ inches bottom, 4½ inches high. Weigh a 100 mg. sample, add 40 c.c. HNO_3 (1.20); place on hot plate and boil until brown fumes have been driven off. Remove from heat, add one small spoonful of PbO_2 (approximately 1 gram); replace on hot plate and boil exactly two minutes. Electric hot plate is the most convenient. (See Photo No. 28.)

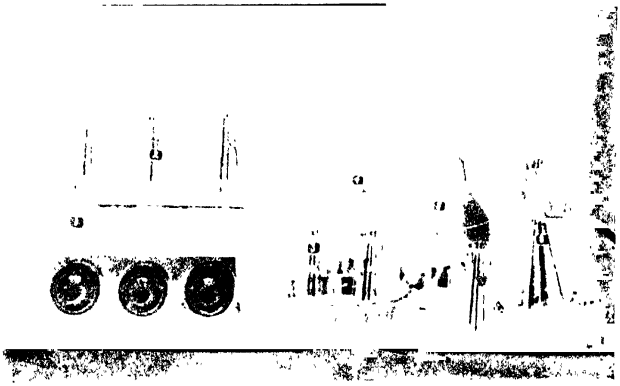

PHOTO No. 28.

Place the flask immediately into a pan of cold water and bring to room temperature as quickly as possible. Using suction, decant the contents of the flask through a porcelain Gooch crucible containing a thin asbestos pad, or through a carbon filter tube with a pad of washed E. & A. asbestos (resting on a perforated porcelain plate) into a 250 c.c. suction flask. Wash filter three times with distilled water, then titrate solution in the same flask to disappearance of pink with standardized sodium arsenite solution. Multiply number of c.c. used by 0.07 and report the product as per cent manganese.

It is not necessary to rinse the original flask after pouring contents on filter. Leave the sediment of excess PbO_2 in the oxidation flask.

EXAMPLE

No. 118 Standard.

7 2 c.c. 2d reading of burette
0 0 c.c. 1st reading of burette

7 2 c.c.
× 07

.504
0.50 Mn.

No. 34 Standard.

12 2 c.c. 2d reading
7 2 c.c. 1st reading

5 0 c.c.
× 07

35 c.c.
0 35 Mn

Preparation of Asbestos.—Fill a 400 c.c. beaker one-third full of E. & A.'s or some other good grade of washed asbestos. Add 200 c.c. distilled water and 100 c.c. H_2SO_4 (1 : 3); bring to a boil; then add $KMnO_4$ solution (25 grams per 1000 c.c.); a few drops at a time, until a slight pink persists after five minutes' boiling; filter on a funnel containing a perforated porcelain disk; using suction. Wash with distilled water until washings are water white. Upset the asbestos plug in funnel several times, so as to give more thorough washing. Place in clean bottle, cover with distilled water and stopper for future use.

Preparing Plug for Filtering.—Transfer some of the soft moist fibers to the filtering crucible, then apply gentle suction while tamping down lightly with a flattened end glass rod. Fill the crucible with distilled water, apply stronger suction and note if the filtrate is clear. If cloudy, repeat filtration of water until clear. The filtering crucible is now ready for use. Have a filter ready before tests come in.

MANGANESE-PERSULPHATE METHOD

Determination of Manganese in the Presence of Chromium. —Dissolve 100 mgs. of sample in a 150 c.c. cone flask 4½ inches high by 2¼ diameter at bottom, by 1¼ inches at top, with 20 c.c. H_2SO_4 (1 : 3); heat on hot plate or stove until dissolved. When dissolved, add 5 c.c. HNO_3 (1.20); boil to expel brown fumes. Remove from heat; add 20 c.c. water; then 10 c.c. $AgNO_3$ (6 grams per liter); then 15 c.c. ammonia persulphate (240 grams per liter); heat moderately (to incipient boiling) until *no more fine bubbles are given off.* Shake flask frequently.

Place in a pan of cold water and cool to room temperature. In plain carbon steel titrate to a straw yellow with sodium arsenite; if chrome is present titrate to a golden yellow color. The number of c.c. consumed multiplied by 0.076 = per cent Mn on 100 mg. sample. Standardize with U. S. Government standard steels of similar composition.

The sodium arsenite solution is the same as used in titration of manganese by PbO_2 method.*

Factor PbO_2 method	0.07 per cent Mn in 100 mg.
Factor persulphate method...	0.076 per cent Mn in 100 mg.

The use of ammonium persulphate and silver nitrate for the determination of manganese in steel was first worked out in the United States by Walters. The silver nitrate acts as an oxygen carrier by the intermediate formation of silver peroxide. The equations showing the action of the persulphate and the arsenious acid and the permanganic acid are given below:

$$2Mn(NO_3)_2+5(NH_4)_2S_2O_8+8H_2O = 2HMnO_4+10(NH_4)HSO_4+4HNO_3. \quad (1)$$

$$4HMnO_4+10As(OH)_3+8HNO_3 = 10H_3AsO_4+4Mn(NO_3)_2+6H_2O. \quad (2)$$

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* Photo. No. 28 shows the oxidizing flasks heated on an electric stove for both the lead peroxide rapid bath test, or in the persulphate method just described. The carbon filter tube is shown at 6 and the oxidizing flask at 2.

contents on filter. Leave the sediment of excess PbO_2 in the oxidation flask.

EXAMPLE

No. 118 Standard.

7.2 c.c. 2d reading of burette
0.0 c.c. 1st reading of burette

7.2 c.c.
× .07

.504
0.50 Mn.

No. 34 Standard.

12.2 c.c. 2d reading
7.2 c.c. 1st reading

5.0 c.c.
× .07

.35 c.c.
0.35 Mn

Preparation of Asbestos.—Fill a 400 c.c. beaker one-third full of E. & A.'s or some other good grade of washed asbestos. Add 200 c.c. distilled water and 100 c.c. H_2SO_4 (1 : 3); bring to a boil; then add $KMnO_4$ solution (25 grams per 1000 c.c.); a few drops at a time, until a slight pink persists after five minutes' boiling; filter on a funnel containing a perforated porcelain disk; using suction. Wash with distilled water until washings are water white. Upset the asbestos plug in funnel several times, so as to give more thorough washing. Place in clean bottle, cover with distilled water and stopper for future use.

Preparing Plug for Filtering.—Transfer some of the soft moist fibers to the filtering crucible, then apply gentle suction while tamping down lightly with a flattened end glass rod. Fill the crucible with distilled water, apply stronger suction and note if the filtrate is clear. If cloudy, repeat filtration of water until clear. The filtering crucible is now ready for use. Have a filter ready before tests come in.

Specially Prepared PbO_2—Weigh five pounds red lead into a 4-liter crock. Add 3000 c.c. HNO_3 (1.13 sp. gr.); stir with a paddle or heavy glass rod. When the residue has a uniform chocolate or brown appearance, let settle; then pour off the liquid. This liquid is largely lead nitrate, and can be concentrated, roasted, and roasted over again. The brown residue is mainly PbO_2.

Fill crock nearly full with distilled water, stir well with paddle, let stand and pour off as before.

Repeat several times, until decanted liquid is only faintly acid or neutral. Transfer residue with a scoop or spatula to a large porcelain dish and evaporate to dryness at 150° C. Powder and put into stoppered bottles.

PbO_2 prepared in this manner is of a light brown color, and settles quickly when used on manganese determinations, and will oxidize manganese completely to as high as 16 per cent in steel. (See method for steel containing 16 per cent of manganese.)

CHAPTER XII

PART VII

THE DETERMINATION OF MANGANESE IN STEELS OF HIGH MANGANESE CONTENT, ACCURATE TO AT LEAST 15 PER CENT MANGANESE, IN THE PRESENCE OF MUCH CHROMIUM

WEIGH 1 gram sample into 400 c.c. beaker; add 30 c.c. H_2SO_4 (1 : 3) and 70 c.c. distilled water and heat mildly until dissolved. Add 20 c.c. HNO_3 (1.20) and boil gently until brown fumes are expelled. Let cool, transfer solution to a 500 c.c. calibrated flask; and after rinsing beaker several times with distilled water, bring volume to 250 c.c.

Make a liquid paste of zinc oxide and water that will just pour; fill a 100 c.c. graduate with the paste, from it, add about 10 c.c. of zinc paste at a time to the flask, shaking thoroughly after each addition until a thin white layer of zinc oxide covers the bottom of the flask on being allowed to settle one minute. *Avoid a large excess of ZnO.* Dilute to the 500 c.c. mark with distilled water; stopper; and mix thoroughly by repeatedly inverting the flask and shaking it. Filter immediately, through dry double 15 cm. filter papers into a dry 400 c.c. beaker; discard the precipitate. Rinse a clean, 50 c.c. pipette twice by drawing about 10 c.c. of the filtrate into it, each time shaking it well. Reject these rinsings.

Now deliver exactly 50 c.c. of the filtrate from this pipette into each of two clean 400-c.c. beakers. Add 200 c.c. HNO_3 (1.20 sp. gr.) and a few grains of pure SiO_2 to each, to prevent violent boiling. Place over good flame; bring to a boil; add 2 grams of specially prepared PbO_2 to each and let boil exactly four minutes. Remove from stove, and add 30 c.c. H_2SO_4 (1 : 3) to each, stir with glass rods; place in a pan of cold running water.

When room temperature is reached, let tests settle for one hour in a cool, dark place, after which time they are ready for titration. Each test represents one-tenth of the original weight.

Titration.—Decant into a clean 600 c.c. beaker all of the solution possible, without disturbing brown lead residue on bottom of beaker. Stir vigorously and add rather rapidly from a burette N/20 ferrous ammonium sulphate until solution in beaker is water white. Back titrate carefully with N/20 $KMnO_4$ solution to the first appearance of a permanent pink. Deduct c.c. permanganate used from c.c. ferrous ammonium sulphate consumed and figure percentage to Mn as shown under "Calculations."

Rapidity of titration gives a better end-point as lead sulphate begins to form in considerable quantity in a few minutes.

Precautions.—(1) Do not mix the H_2SO_4 and the nitric acid before adding the acids to the drillings. Put the sulphuric acid on first, and then add the nitric acid, only, after the sulphuric acid has ceased its action. The purpose of this procedure is to remove as far as possible all of the carbon and carbides before the nitric can act on them. If the carbon gets into solution, the complete oxidation of the manganese to permanganic acid is interfered with.

(2) Remove the iron with the zinc oxide, whether there is chrome present, or not, when the manganese is from 3 per cent to 15 per cent. There is evidence that the oxidation of high per cents of manganese, in steel, to permanganic acid, by means of lead peroxide, is most successful when the iron is first removed by zinc oxide. The author is not prepared to state whether this is due to the absence of the iron or due to the precipitated iron sweeping out the last traces of carbon. The nitric acid may put carbon into solution when it attacks the carbides that the sulphuric acid failed to dissipate as gas before the nitric acid was added.

STANDARDS

400 mg $KMnO_4$ 1 gm. plain steel	(A) 14 per cent Mn approximately
200 mg. $KMnO_4$ 100 mg. $K_2Cr_2O_7$ 1 gm. plain steel	(B) 7 per cent Mn approximately 3.5 per cent Cr approximately

Put standards through operations simultaneously with the tests. A high manganese steel on which the manganese has been carefully determined gravimetrically may be used for a standard also, if preferred.

Standardization and Calculations

KMnO$_4$			Fe. Am. Sul.
7.3	200 mg. KMnO$_4$ 100 mg. K$_2$Cr$_2$O$_7$ 1 gm. steel	(B) 1/10	44 8
2 9			27 6
4.4	(B) is diluted to 500 c.c.		17 2 −4 4
			12.8 c.c.

50 c.c. of (B) run as a standard.

3476 Mn in 1 gm. KMnO$_4$
2
.06952 Mn added
0022 Mn in steel
10) 07172
.007172

00056
12 8) .007172
640
772
768
4

1 c.c. = 0.56 per cent Mn on 100 mg. sample

KMnO$_4$	Standard steel 13 52% Mn	
2 9		
0.0	000563	Fe. Am. Sul.
2.9	24) 013520	27 5
	120	.06
	152	26 9
	144	−2 9
	80	24.0 c.c.
	72	
	8	

1 c.c. = 0.563 per cent Mn on 100 mg. sample

KMnO$_4$	Sample No. 1 100 mg.	Fe. Am. Sul.
		61 4
7.0		44.8
2.9	7.02 per cent Mn	16.6
4.1		−4 1
		12 5 c.c.
		.5615 Mn factor
		7.018 % Mn

CHAPTER XII

PART VIII

SILICON IN PIG IRON, STEEL AND MUCK BAR

WEIGH 1.5 grams of pig iron into a No. 2 dish. Add 15 c.c. 1 : 3 sulphuric acid * plus 10 c.c. water. Weigh 5 grams of low silicon steel or 3 grams of high silicon steel, i.e., silicon content of 0.1 per cent and over, into a No. 5 dish. Add 45 c.c. 1 : 3 sulphuric acid and 25 c.c. of water. Warm gently until all metal is in solution, adding more water if necessary, should sulphate of iron form before effervescence is over. When the iron is in solution evaporate the pig iron and higher carbon steels directly to thick fumes of sulphuric anhydride without removing the covers.

Low carbon steels and chrome steels of 1 per cent chromium and over will bump and spurt from under the covers if attempt be made to evaporate them rapidly over the bare flame of the Argand burner. In such cases the covers are rinsed off into the dishes, and the contents of the latter are evaporated to thick fumes on a graphite or sand bath. (See page 448, view 43.)

For effecting the solution of the iron and the evaporation of fumes with covers on, an apparatus consisting of a stand of twelve Argand burners covered with a copper-rimmed asbestos board of twelve holes are used. (See Fig. 21, page 310.)

Having evaporated the samples to fumes, the dishes are cooled and filled conveniently full of distilled water. They are put on the heating stand; the contents heated and stirred until all of the sulphate of iron is in solution. Ashless paper pulp is mixed with the solutions, which are then filtered through 11

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* Use rubber stoppers in reagent bottles that are in constant use in routine silicon work, as during continued handling the glass stoppers are struck against the necks of the bottles and small chips of glass are knocked off into the acids, causing high results.

cm. ashless filters; the silicious residues washed free from iron test with 1 : 10 hydrochloric acid and then free of acid with water. Potassium sulphocyanate is used in testing for the presence of iron. Wash acid and wash water are applied cold.

The washed residues are ignited in a muffle furnace until pure white.* The residues may retain a reddish tint due to iron, or may be colored gray from presence of chromium or copper oxides, or yellow owing to the presence of small quantities of tungsten or vanadium. In such event after having been weighed they should be evaporated to dryness with a few drops of sulphuric acid and 10 c.c. of c.p. hydrofluoric acid. They are then ignited and weighed again, and the silicon content is calculated from the loss of weight, which multiplied by 46.93 and divided by the weight taken, yields the percentage of silicon.

When chromium is present, to the extent of 1 per cent, the silica residue can be freed sufficiently from chromium to make a subsequent evaporation with hydrofluoric and sulphuric acids unnecessary by boiling the fumed sulphate residue for ten minutes with a mixture of 75 c.c. of 1 : 1 hydrochloric acid and 75 c.c. of water. Then filter and wash as before.†

The ignited residues are cooled in a desiccator, weighed, multiplied by 46.93 and divided by the weight taken.

The silicious residues obtained by this method, or any other of the variations that are in vogue, are liable to be contaminated with titanium and aluminum, especially in pig iron. Hence all silica residues, for strictest accuracy, should be evaporated with an excess of hydrofluoric acid and two or three drops of sulphuric acid, then ignited and weighed again, multiplying the loss of weight by the usual factor, and dividing by the weight taken to obtain the percentage of silicon.

ROUTINE METHOD FOR PLAIN STEEL, PIG IRON, ETC.

It is the practice in probably all large steel works laboratories to burn off the carbonaceous matter from the washed siliceous residue in an unweighed crucible. If the ash is pure white, instead of weighing the crucible and ash together, the ash, only, is brushed out of the crucible onto the glass scale pan and weighed. This permits the use of a refractory crucible such as porcelain or fused silica. The author prefers to use a zirconia composition crucible, which can be referred to as a silicon cup.

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* The author uses an electrically heated muffle ventilated by a slow stream of compressed air.

† For close work it is always advisable to use the hydrofluoric acid when chromium is present.

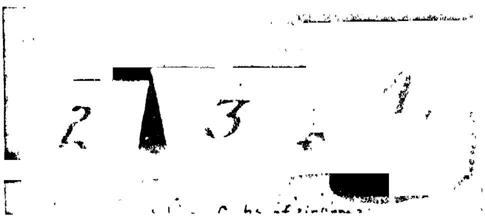

Photo No. 29.

The most convenient size is $1\frac{1}{2}$ inches outside diameter at the top; 1 inch bottom diameter and $1\frac{1}{4}$ inches high. In case the ash is not white, it can be transferred to a platinum crucible; weighed; and evaporated with H_2SO_4 and HF as already described. The silicon cup is shown in Photo No. 29, at *2*.

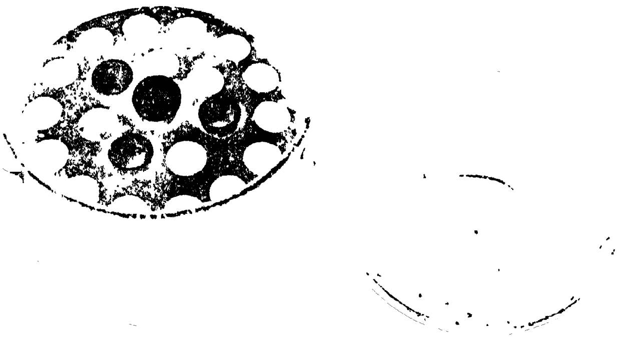

Photo C. Holder for Silicon Cups

CHAPTER XII

PART IX

THE ANALYSIS OF CALCIUM ELECTRO-SILICON

0.9 or 1.0 gram of the floured sample is fused with 20 grams of anhydrous sodium carbonate ground with 2 grams of niter in a platinum crucible. The analysis is proceeded with as in crucible slag (page 132), obtaining residues *A* and *B*, which contain all of the silicic acid and perhaps a small portion of the calcium, iron, etc. This residue is weighed and hydrofluoric acid is added to it very slowly at first and finally enough of this acid to fill the crucible two-thirds full. Before the HF, 10 drops of conc. sulphuric acid are added. Then evaporation to fumes follows and the silicon is finished as in steels. Where such large amounts of silica are evaporated it is well to add more HF and sulphuric acid and repeat the volatilization to make sure that all of the silica has been removed. The stain or residue remaining in the crucible after these evaporations is fused with a gram of sodium carbonate, dissolved out with HCl and added to the combined filtrates from *A* and *B* which will now contain all of the iron, aluminum manganese, calcium and magnesium. A double basic acetate separation of the iron as given on pages 244 and 245 is made. The acetate precipitate from the second precipitation is ignited, dissolved in HCl, precipitated with ammonia, washed, ignited, and weighed as oxides of iron and aluminum. These oxides are then dissolved in HCl and the solution is divided into two equal parts. One-half is reduced with stannous chloride and finished for iron as in iron ore. The other half is converted into nitrate and finished for phosphorus as in steel. The iron is multiplied by two, calculated to ferric oxide and deducted from the total oxides. The phosphorus is also multiplied by two, calculated to P_2O_5 and deducted from the total oxides. The remainder after these deductions is calculated to metallic aluminum.

The filtrates from the two basic acetate precipitations contain all of the calcium which is precipitated with ammonium oxalate and finished in the usual way as in limestone. The manganese is obtained as in tungsten, page 77.

ANALYSIS

	Per Cent		Per Cent
Silicon	58 48	Calcium	30 86
Iron	7 08	Carbon	0 80
Aluminum	2 41	Manganese	0 06

The carbon is gotten by ignition of 0.5 gram of the sample with 4 grams of red lead, or litharge, in the electric furnace.

CHAPTER XIII

PART I

THE DETERMINATION OF URANIUM IN FERRO-URANIUM, CARNOTITE ORE AND MIXTURES OF IRON, VANADIUM, URANIUM AND ALUMINUM

THE determination of uranium in ores and ferro-alloys is usually complicated by the presence of vanadium and aluminum. The author has encountered so-called ferro-uranium containing as much as from 15 to 20 per cent of aluminum in several instances. Vanadium was always present from 2 or 3 per cent to as high as 28 per cent.

The scheme of titrating the uranium and vanadium together by reducing both elements in sulphuric acid solution with aluminum was tried as recommended by some writers. In this method the total amount of the permanganate standard required to reoxidize both elements so as to produce a slight permanent pink color, is noted. Then the vanadium, alone, is reduced, this time to V_2O_4 only, by adding an excess of sulphurous acid (SO_2) and boiling off the excess of the latter. The vanadium is then oxidized back until a slight permanent pink is again obtained. The number of c.c. of the $KMnO_4$ required in this second titration is multiplied by three and deducted from the amount of the permanganate used in the first titration. The remainder is multiplied by the uranium value of the permanganate, thus obtaining the uranium. In the author's hands the results were discordant whether the reduction was accomplished by aluminum or zinc. The more vanadium present the worse disagreements, and the less vanadium, the more nearly the true uranium was obtained. With uranium, alone, the reduction with permanganate is entirely satisfactory.

During these experiments the writer tried hydrogen sulphide as a reducing medium and found that H_2S reduces both vanadium and iron but *does not reduce the uranium.* This afforded a way of determining the vanadium in the presence of the uranium but has no advantage over the method of the writer, to be described. The H_2S reduction makes it possible to determine both iron and vanadium in the presence of uranium, in fact to determine all three elements.[c] The uranium and iron together with the vanadium carried by them can be precipitated by a slight excess of ammonia; washed with ammonium nitrate water; ignited at a low red heat; moistened with conc. nitric acid; ignited again at a low red; cooled and weighed as Fe_2O_3, U_3O_8 and some V_2O_5 (all of the V_2O_5, if sufficient of the Fe and U be present). The weighed oxides are dissolved in HCl; evaporated with 40 c.c. of 1 : 3 H_2SO_4 to thick fumes; dissolved in 150 c.c. of water and the vanadium and iron in the mixture determined as given on page 38, reducing with H_2S. The Fe and V so found are calculated to the proper oxides and deducted from the weight of the total oxides above mentioned and the uranium oxide is thus obtained by difference. Similarly, U and Fe alone can be analyzed, getting the iron by the H_2S reduction and the uranium by difference. Also should aluminum be present, the total oxides, after being weighed, can be dissolved, the solution be divided into two equal parts and one part analyzed as above for the Fe_2O_3 and V_2O_5, and the other part analyzed for aluminum oxide as given in the method about to be described. Deduct twice the $Al_2O_3+Fe_2O_3+V_2O_5$ found from the weight of the total $Al_2O_3+U_3O_8+V_2O_5+Fe_2O_3$, obtaining the U_3O_8 by difference.

The author devised, and tested the following method for the determination of uranium in carnotite, ferro-uranium, and steel: For carnotite ores containing, as they usually do, from 1 to 4 per cent of U_3O_8 weigh 2 grams and 3 grams for a check. For ferro-uranium do not take over 1 gram, and a half gram for a check. Dissolve or extract the samples, first with 100 c.c. of conc. nitric acid for an hour. Evaporate to dryness in the casserole, using a porcelain casserole of 4½ inches diameter. Take up in 100 c.c. of conc. HCl, evaporate to 20 c.c., dilute with 50 c.c. of water and filter out the insoluble residue consisting mainly of silica. Wash with dilute HCl about fifty times. Dilute to 300 c.c.; nearly neutralize with ammonia; and pass H_2S in hot solution to remove any Mo, Pb, Sn, Cu, As, Bi, or Sb that may be present.

Filter; wash with H_2S water, thoroughly, and evaporate the filtrate and washings to 20 c.c.; add an excess of chlorate of potassium, about 1 gram to destroy the H_2S, also 50 c.c. of HCl, conc., and heat, covered, until all spraying is over and evaporate to 20 c.c. Transfer to an 800 c.c. beaker; add sodium peroxide from a porcelain spoon to the 300 c.c. solution in the beaker, until a slight excess is obtained. (It should be said that the above mentioned insoluble residue is evaporated with an excess of HF and 10 drops of conc. H_2SO_4 and the remaining residue is fused with sodium carbonate; the fusion is dissolved out with HCl and added to the main solution in the beaker before commencing the addition of the sodium peroxide.) When an excess of peroxide has been added to the solution in the 800 c.c. beaker, then 5 grams of ammonium carbonate are added to the alkaline solution; and 5 grams of sodium carbonate are put in, and last of all, 5 grams excess of sodium peroxide are added. The solution is now just brought to incipient boiling, and immediately removed from the flame; cooled; paper pulp is added and the solution is filtered from the iron through 15 cm. double filters into 800 c.c. beakers. The iron on the filter is washed with a mixture consisting of 5 grams each of sodium and ammonium carbonates, dissolved in 500 c.c. of water. The filtrate and washings, which should have a volume of not less than 400 c.c., are now neutralized with 1 : 1 HCl, added until the solution no longer immediately turns a narrow strip of turmeric paper, to the faintest brown. If there be alumina present to the extent of even a half per cent, it will have clouded the solution long before the turmeric ceases to be affected by the solution. Let the latter stand for at least an hour and then the aluminum can be filtered out, and washed with ammonium nitrate as given previously (5 grams of the salt to 500 c.c. of water).

If the titration with acid is carefully done the filtrate and washings will not contain aluminum even though there be in the solution the equivalent of 0.100 gram of Al. The filtrate and washings from the aluminum will contain all of the U and much of the V, if the iron present does not exceed more than the equivalent of 0.100 gram of iron. The iron can be dissolved off the filter, peroxidized a second time as before and the alkaline filtrate and washings obtained, keeping them separate from the filtrate and washings obtained from the first peroxidation. These two filtrates and washings are then made entirely acid after the removal of the aluminum, and boiled for one hour, or until all CO_2 is removed from the solution, which will be accomplished when there are no longer any more lines, or fine threads of bubbles coming up through the solution. Then the uranium together with considerable vanadium is precipitated out with a *slight* excess of ammonia. The solution is boiled gently for a half hour. If much vanadium is present, the precipitate will be more of a green than a yellow; but if much uranium and little vanadium be present, then the precipitate will take on a bright yellow color, especially after heating for a time. The precipitate which consists mainly of uranium vanadate is filtered off and washed with the ammonium nitrate wash (5 grams to 500 c.c. of water). After a few washings, the precipitate is dissolved off the filter to get rid of any occluded salts, reprecipitated, and washed as before. The precipitate is now ignited in a platinum crucible, or a porcelain one if the platinum one is not available, and ignited at a low red heat, after the paper has been smoked off. The ash is moistened with a few drops of conc. nitric acid, and again heated to a low red heat; cooled; and weighed as U_3O_8 plus V_2O_5. The weighed oxides are dissolved * in conc. H_2SO_4; transferred to small casseroles and evaporated low with 50 c.c. of HCl. This solution is then evaporated to thick fumes, with 40 c.c. of 1 : 3 H_2SO_4; cooled; diluted with water; filtered from the small amount of silica usually present which is washed with dilute sulphuric acid; ignited and weighed; and deducted from the U_3O_8 plus V_2O_5. The filtrate and washings from this silica contain the vanadium that was precipitated with the uranium. Owing to the evaporation with the large excess of HCl, the vanadium is now reduced to V_2O_4. It can be titrated to a permenent pink with the standard permanganate solution, and the vanadium so found is calculated to V_2O_5 and subtracted from the silica-free weight of the above oxides, thus giving the uranium by difference. Also the filtrate and washings from the small amount of silica can be heated to boiling and permanganate solution added cautiously so as to maintain a pink solution but not in such excess as to produce a heavy precipitate of manganese oxide as that would make a filtration necessary.* The boiling is continued for twenty minutes. If the solution still remains pink with perhaps a very slight precipitate of the manganese oxide, then it is certain that all organic matter that may have crept in during the analysis is rendered harmless as far as affecting the permanganate standard during the subsequent titration is concerned. The ferrous ammonium sulphate standard is now added to the hot solution until the pink color is just removed and any slight cloud of precipitated manganese oxide is also dissolved, leaving the solution perfectly clear. The solutions of the tests are now cooled, and an excess of the permanganate standard is added to all of them. Then one of them is titrated drop by drop with the sulphate standard until three drops at room temperature give but a faint pink that remains practically unchanged for one minute. This is the starting point of the titration with the ferrous ammonium sulphate standard. The volume should now be not over 200 c.c. Add 2½ c.c. of the ferricyanide indicator (5 grams of the salt dissolved in 130 c.c. of water) and then the ferrous ammonium sulphate standard with vigorous stirring until three drops change the dark green color that forms to a distinct blue, i.e., to the first real blue. The number of c.c. of the sulphate standard required to produce this blue, after the addition of the indicator, multiplied by the vanadium value of the sulphate gives the vanadium that was carried out with the uranium. It is calculated to V_2O_5 and the uranium is thus obtained by difference. The U_3O_8 so found can be calculated to metallic U by the factor 0.8482. To standardize the permanganate and sulphate standards for vanadium, it is convenient to weigh 0.08 and 0.04 gram of vanadium pentoxide of known purity into small casseroles; dissolve in 60 c.c. of conc. HCl; evaporate low; fume with 40 c.c. of 1 : 3 H_2SO_4 and carry through all of the operations leading up to the titration with $KMnO_4$ and the final titration with the sulphate. This will give the blank to deduct from each method of titration of the vanadium.

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* Do not use HCl at this point, as chlorine would be generated and the platinum badly attacked. Use 10 c.c. conc H_2SO_4 and heat for an hour, or until dissolved.

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* Of course there is no objection to boiling with an excess of the manganese oxide except the extra operation involved. Indeed the author has had cases where, owing to carbonaceous matter having gotten into the work, probably by extraction from filter papers, or mechanically, it was deemed advisable to boil with an excess of permanganate sufficient to produce a precipitate that remained even after a half hour of boiling. This brown oxide is filtered out through a porous thimble and the vanadium titrated exactly as described on page 22.

For checking methods and manipulations the writer used c.p. uranium nitrate and uranium acetate $UO_2(NO_3)_2+6H_2O$ and $UO_2(C_2H_3O_2)_2+2H_2O$, respectively.

A mixture that approximates to the general run of carnotite ores of the Colorado mines is 0.100 gram of uranium nitrate, 0.100 gram of the Sibley iron ore standard; 0.050 gram of aluminum, and 0.040 gram of V_2O_5. (The latter can be obtained of 99.5 per cent V_2O_5.) As a further check, the author often runs a mixture of double the above amounts of uranium salt, the oxide of vanadium, and iron ore. These mixtures are put through all of the operations described.

Calculations.—For the benefit of those who wish to try the reduction with aluminum to check the purity of uranium nitrate, or who may wish to assay uranium obtained from a source that is free of vanadium, the method in general is to convert to sulphates, and heat in cone flasks in the presence of an excess of from 20 to 30 c.c. of conc. H_2SO_4 diluted to 100 c.c. with water. A coil of 18 gauge aluminum wire of $\frac{5}{16}$ inch diameter and about 7 inches long * is placed in the solution, and the latter is heated to nearly boiling for two hours with a stream of purified CO_2 passing through a perforated watch glass into the cone flask to prevent the entrance of air. The CO_2 is generated by the action of HCl (1 : 1) on marble and passes through a wash bottle containing an inch of water and then through another bottle containing a similar depth of a saturated solution of sodium carbonate. After the two hours' reduction, the solution is cooled with CO_2 passing, and when cold the aluminum coil is removed and the solution is titrated with N/40 $KMnO_4$ to a slight permanent pink. A blank is also run at the same time and deducted. A solution of N/40 should equal 0.00298 gram U per c.c. The equation is

$$2KMnO_4+5UO_2(SO_3)_2+2H_2O = 2KHSO_4+2MnSO_4+5UO_3(SO_3)+H_2SO_4.$$

The permanganate is standardized with sodium oxalate (see page 20).

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* See Photo No. 30.

Photo No. 30.

By the above equation we see that 2 gram molecules of $KMnO_4$ equal 5 gram atoms of U. On page 463 it is explained that $\frac{1}{5}$ of the gram molecule of permanganate constitutes its normal solution when dissolved in a liter volume. Hence, $2KMnO_4 = 5U$, or $KMnO_4 = \frac{5U}{2}$, so that $\frac{1}{5}$ of the gram molecular weight or normal $KMnO_4$ would equal $\frac{1}{2}$ the gram molecular weight of uranium or 119.25 grams of U. Therefore 1 c.c. of the N/40 $KMnO_4$ is equal to $\frac{119.25}{40.000}$, or 0.00298 gram of U. Having found by titration the value of the permanganate standard per c.c. in sodium oxalate as given on page 20, the following give the values of the N/40 permanganate in U, V, and Fe.

The value of N/40 $KMnO_4$ per c.c. in gram of sodium oxalate multiplied by $\frac{238.5}{134}$ equals its value in gram of U per c c.

by $\frac{102.0}{134}$ equals its value in gram of V per c.c.

by $\frac{111.7}{134}$ equals its value in gram of Fe per c.c.

The percentage of uranium in uranium nitrate is 47.45.

The percentage of uranium in uranium acetate is 56.17.

The percentage of uranium in uranoso-uranic oxide (U_3O_8) is 84.825.

The percentage of vanadium in vanadium pentoxide is 56.04.

From a standardization as above, the author, for example, found that 1 c.c. of N/40 $KMnO_4$ equals 0.00167 gram of sodium oxalate.

1 c.c. of N/40 $KMnO_4$ equals 0.00297 gram of uranium.

1 c.c. of N/40 $KMnO_4$ equals 0.001276 gram of vanadium.

The following are the calculations for an actual analysis of a mixture: 0.100 gram of uranium nitrate crystals, 0.100 gram of the Sibley iron ore standard, 0.05 gram of metallic aluminum, and 0.040 gram of V_2O_5 of 99.5 per cent purity were put through all of the operations in the method as described and the following analytical data were obtained:

(1) 58.8 c.c. of sulphate were required to remove all pink and brown tints from 60 c.c. of the $KMnO_4$ standard (N/40)

placed in a beaker with 40 c.c. of 1 : 3 sulphuric acid and 200 c.c. of distilled water. As 1 c.c. of the N/40 $KMnO_4$ was found equal to 0.001276 gram of V then 1 c.c. of the ferrous ammonium sulphate standard is equal to 0.001276×60 divided by 58.8 or 0.0013 gram of V.

(2) The $U_3O_8+V_2O_5$ obtained, in the course of the analysis, from the above mixture weighed 0.076 gram after deducting 0.0014 gram of silica found in it on dissolving in HCl.

(3) Beginning at the point where the U_3O_8 plus V_2O_5 were dissolved in HCl; evaporated with 40 c.c. of 1 : 3 H_2SO_4 to thick fumes, etc., 0.020 and 0.040 gram of the V_2O_5, alone, were put through all of the subsequent operations and the vanadium therein was titrated with the sulphate standard as already described. The 0.020 gram required 10.1 c.c. of the sulphate to produce the blue end-point, and the 0.040 consumed 18.8 c.c. (Blank and all.) The 0.020 gram of V_2O_5 contains $0.020 \times 0.995 \times 0.5604 = 0.01116$ gram V. Now we saw by (1) that the sulphate standard has a value of 1 c.c. equals 0.0013 gram of V, hence the sulphate required to unite with the vanadium present will equal 0.001115 divided by 0.0013 or 8.6 c.c. This gives 10.1 c.c. minus 8.6 c.c. or a blank of 1.5 c.c. to be deducted from all tests.

(4) The V_2O_5 in (2) was determined in like manner and found to require 9.5 c.c. of the sulphate. We have just seen that the calculated blank is 1.5 c.c., therefore the actual V in (2) required 9.5 minus 1.5, or 8 c.c. Then the V_2O_5 in (2) is equal to $0.0013 \times 8 \div 0.5604$ or 0.0185 gram. Hence the U_3O_8 in (2) equals $0.076-0.0185$ or 0.0575, which is equivalent to 0.0487 gram of uranium. The uranium contained in the uranium nitrate taken equals 0.100×0.4745 or 0.04745 gram of uranium. This gives an excess of 0.0012 gram of U found, which was in all probability due to the presence of a little Al that was not removed by the neutralization with the 1 : 1 HCl. The author would recommend that the operator exercise great care in the neutralization. The acid should be added until, as already stated, a narrow strip of turmeric paper dipped into solution does not show any more change than a similar strip dipped in water. It is also advisable, for close work, to allow the neutralized solution to stand for twelve hours before filtering out the aluminum hydroxide.

It must be remembered that when a very large quantity of iron, for instance 0.400 gram of iron, is to be separated from much uranium, say about 0.200 gram of U and 0.100 gram of Al, then at least three peroxidations will be required, made as described under carnotite, to remove all of the U and Al away from the iron. Then when the Al is separated from the U by the acid precipitation, the Al is almost certain to carry out with it 2 or 3 mgs. of U_3O_8. This latter can be removed by redissolving the Al in the hot 1 : 1 HCl; the solution of the Al is treated with an excess of sodium peroxide, i.e., the peroxide is added to it in a liter boiling flask to strong alkaline reaction; then add 5 grams each of sodium carbonate, and ammonium carbonate, and 5 grams sodium peroxide. Bring just to the boil; cool and precipitate, as already described, to the turmeric neutral point with 1 : 1 HCl; let stand for twelve hours and filter out the Al which will now be free of U. The filtrate from the Al is made acid; boiled until free of CO_2; and the small amount of U is precipitated with ammonia in slight excess, boiling gently for thirty minutes. The U is filtered out; and added to the main portion of the U before it is precipitated with ammonia the first time.

Most ferro-uranium and ferro-uranium-vanadium-aluminum alloys will dissolve in a mixture of HCl and HNO_3, but the author analyzed one such alloy that contained 15 per cent of silicon that could be decomposed only by fusing it twice with sodium peroxide. The following results attest the accuracy of the method:

Uranium Added	Uranium Found	Uranium Added	Uranium Found
Gram	Gram	Gram	Gram
0 047	0 048	0 071	0 0729
0 047	0 047	0 047	0 0468
0.094	0.0948	0.094	0.0950

DETERMINATION OF URANIUM IN STEEL

The feature of the following method is to remove the bulk of the iron from the uranium, zirconium, and aluminum by fractional precipitation by ammonia. The analysis can

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then be proceeded with in a simple and accurate way. The separation of the bulk of the iron is based on the fact that when ammonia is added to iron in the ferrous state the unoxidized iron is first converted to double sulphate of ferrous iron and ammonium and remains in solution. By adding the ammonia very slowly with constant stirring a point in the neutralization is reached where a slight reddish precipitate forms. On the addition of a few drops more of ammonia this reddish precipitate darkens. At this stage all the aluminum, zirconium, uranium, etc., is precipitated, while 99 per cent of the total iron remains in solution as double sulphate and is removed by filtration. By actual test with 10 grams of plain steel to which uranium salt was added, over 99 per cent of the iron remained in solution.

Uranium in Plain Steel.—Dissolve on a low flame 5 grams of drillings in 50 c.c. 1 : 3 sulphuric acid diluted with 50 c.c. of water, using a 600 c.c. beaker. For steel containing less than 0.1 per cent uranium use 10 grams of sample. When action is over, filter off the insoluble residue, which is mainly carbide, and wash it twenty-five times with dilute sulphuric wash (25 c.c. of 1 : 3 H_2SO_4 diluted with water to 600 c.c.). Call this filtrate and washings *A*. The insoluble residue may contain U, so it must be ashed in a platinum crucible at a low heat; cooled; 6 c.c. of HF plus 6 c.c. of 1 : 3 sulphuric acid added; evaporated to thick fumes of SO_3; cooled; a little water added; heated to dissolve the sulphates and the clear solution is added to *A*. Then dilute to 250 c.c. volume with water and add 1 : 1 ammonia with constant stirring until a slight precipitate forms. Then continue to add ammonia drop by drop until the precipitate just begins to take on a blackish tint. At this stage all the uranium has been precipitated with only a small portion of the iron.

To assure a complete precipitation of the uranium add about 10 more drops, but do not exceed 10 drops, as excess ammonia only brings down a greater bulk of the iron. Filter off the precipitate at once on a double 15 c.c. filter paper and redissolve it in 50 c.c. 1 : 1 HCl. First warm up the acid in the beaker to dissolve any iron that sticks to the sides; then pour the hot acid on the precipitate, catching the filtrate in a 600 c.c. beaker. Pour hot filtrate on the filter two or three times until all the iron is in solution. Wash the filter paper about twenty-five times with dilute HCl wash (1 : 40). Now peroxidize the filtrate and washings by adding slowly, with a porcelain spoon, about 1 gram of sodium peroxide at a time. After each addition wash off the sides of the beaker with water and stir the solution well. Keep on peroxidizing until all the iron is precipitated and the solution is alkaline when tested with red litmus paper.

Now add about 5 grams of sodium carbonate and 5 grams of ammonium carbonate to keep the uranium in solution. Stir well and bring it just to a boil. Filter off the iron and wash it about twenty-five times with sodium and ammonium carbonate wash (2 grams of Na_2CO_3 and 2 grams of $(NH_4)_2CO_3$ dissolved in 600 c.c. of water). To the filtrate which contains all the uranium add 1 : 1 HCl with stirring, till solution no longer turns turmeric paper even a faint brown, but still reacts alkaline when tested with red litmus paper. Keep the beaker covered when adding the acid, as the effervescence is very strong, especially toward the end of the neutralization. Boil off the CO_2 and then add slowly with stirring (keeping the beaker covered) 1 : 1 HCl till the solution is slightly acid. No more effervescence at this stage, but the acid falls down to the bottom of the beaker without action.

Boil the acid solution for half an hour to remove CO_2 and after it has been cooled add 5 grams of ammonium phosphate, $(NH_4)_2HPO_4$; stir till dissolved; then add 1 : 1 ammonia till it smells ammoniacal and add 1 : 1 acetic acid till the solution is acid; now add 5 c.c. acetic acid in excess. The acetic acid keeps the chromium and vanadium in solution. Chromium does not interfere with the uranium titration, but vanadium interferes greatly.

After a few hours, filter off the uranium and wash it about forty times with acetic wash (5 c.c. of ammonium phosphate, 10 c.c. 1 : 3 H_2SO_4 diluted with 100 c.c. of water, stir till dissolved, make it slightly ammoniacal and then acid with acetic acid 5 c.c. in excess. Dilute with water to 600 c.c.). Redissolve the uranium in 50 c.c. hot 1 : 3 H_2SO_4 by pouring the hot acid back and forth two or three times on the precipitate, catching the filtrate in a 400 c.c. beaker.

Wash the filter paper about thirty times with dilute H_2SO_4 water. In high vanadium steel it is better to test for vanadium by adding 5 c.c. of H_2O_2 to the solution and noticing whether it changes to brown; if it does, repeat the ammonium phosphate precipitation to remove the vanadium. If the solution does not change in color, bring it to a boil; then add several

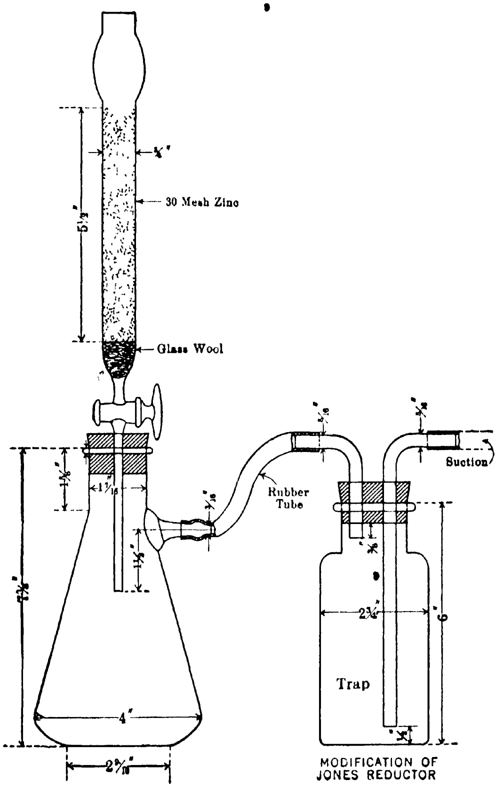

Fig. 31.

drops of $KMnO_4$ until a pink color is formed that will not fade after fifteen minutes' boiling. Cool the oxidized solution to room temperature. Now reduce the uranium by passing it slowly through a zinc reductor, Fig. 31, and immediately titrate the reduced solution with a standard $KMnO_4$ solution to the first appearance of pink that spreads all through the solution. If there is any vanadium in the solution at this stage the pink will disappear in about five seconds instead of holding one minute. Any more permanganate added that disappears after five seconds' standing is due to vanadium that has been carried over as phosphate.

Jones Reductor.—The column of zinc in the reductor, Fig. 31, rests on a $\frac{3}{4}$-inch plug of glass wool. The zinc column is $5\frac{1}{2}$ inches long by $\frac{3}{4}$ inch in diameter consisting of 30-mesh grains of amalgamated zinc. The amalgamation is accomplished by stirring the 30-mesh zinc under a covering of mercuric chloride solution made by dissolving 50 grams of $HgCl_2$ in 1000 c.c. of water. The zinc after amalgamation is washed with distilled water by decantation in a beaker until free of excess mercuric chloride, when it is ready for use.

A trap jar is placed between the filtering flask and the suction to prevent back pressure which would carry water over from the suction pump into the flask which holds the filtered, reduced solution of uranium. The volume of the uranium solution to be reduced is about 50 c.c. This is passed through reductor slowly, i.e., at the rate of 50 c.c. per ten minutes.

After passing the solution through the reductor, wash the zinc with dilute H_2SO_4 (1 : 6) three times, 10 c.c. each time, and then three times more with 10 c.c. of water each time; drawing off each washing completely before adding next washing. The volume before titrating is about 100 to 110 c.c.

For convenient calculation 2.29 grams $KMnO_4$ are dissolved in distilled water and diluted to 4 liters

1 c.c. $KMnO_4$ standard = 0.002169 gram U.

1 c.c. $KMnO_4$ standard = 0.001014 gram Fe.

The standard $KMnO_4$ can be checked for its uranium and iron value by titrating it against sodium oxalate.

URANIUM IN CHROME-TUNGSTEN STEEL

Dissolve 5 grams of steel in 50 c.c. of 1 : 3 H_2SO_4 diluted with 50 c.c. of water; after action is over, filter off the insoluble residue and dilute the filtrate to about 250 c.c. volume with water. Now add 1 : 1 ammonium with constant stirring until the precipitate at first takes a reddish tint, next changing to a blackish and finally to a bluish-whitish. At this stage add about 2 c.c. of ammonia with stirring to complete the precipitation of all the uranium in the filtrate with only a small portion of the iron. Filter it off at once and finish as in plain uranium steel.

The insoluble tungsten and chromium carbide residue on the filter was found to contain some of the uranium. Wash it off the filter paper with dilute sulphuric acid into the original beaker, heat it, and then oxidize it with 30 c.c. of 1.20 nitric acid. Keep on heating on a low flame until the residue is bright yellow. Filter off the tungsten, wash it about twenty-five times with dilute H_2SO_4 wash; and peroxidize the filtrate with sodium peroxide to separate the uranium from the iron. Catch the uranium filtrate from the main peroxidation and that from peroxidation of the insoluble residue in the same 800 c.c. beaker and finish as in plain steel.

A variety of mixtures were tested by adding different portions of uranium acetate (56.13 per cent U). The results are given below:

TABLE SHOWING URANIUM ADDED AND FOUND TO 10-GRAM SAMPLE OF PLAIN STEEL

Added, Gram Uranium	Found, Gram Uranium
0 0112	0 0119
0 0143	0 0143
0 0168	0 0169
0 0280	0 0286
0 0561	0 0573
0 0056	0 0055
0 0084	0 0085

Ten grams of plain carbon steel—no uranium added.

$KMnO_4$ 1 2 c.c. reading of burette after titration.
$KMnO_4$ 0 0 c.c. reading of burette before titration.

$KMnO_4$ 1 2 c.c. = blank which is deducted.

Uranium, chromium and iron mixture, chromium added as $K_2Cr_2O_7$ to 10-gram sample of plain steel before dissolving same in H_2SO_4.

TABLE SHOWING URANIUM ADDED AND FOUND TO 10-GRAM SAMPLE OF STEEL

Added, Gram	Found, Gram
0.0056	0.0057
0.0084	0.0085
0.0280	0.0286
0.0561	0.0558

TABLE SHOWING URANIUM ADDED AND FOUND TO 5-GRAM SAMPLE OF TUNGSTEN, CHROME, VANADIUM STEEL

Added, Gram	Found, Gram
0.0112	0.0113
0.0280	0.0278
0.0561	0.0575

Five grams—no uranium added.

1.8 c.c. reading of burette after titration.
0.0 c.c. reading of burette before titration.
———
1.8 c.c. = blank which is deducted.

About 80 per cent of the iron is removed by ammonia precipitation in the filtrate when large amounts of carbides of tungsten, chrome, and vanadium are present, as was found by actual test. The bulk of the 20 per cent of iron that remains to be separated by peroxidation is found in the carbide residues of these steels.

CHAPTER XIII

PART II

THE DETERMINATION OF VANADIUM IN SANDSTONES CONTAINING CARNOTITE, ROSCOELITE, AND CALCIUM VANADATE, ETC.

(A) IF the sandstone contains about 3 per cent V then take 3 grams of the finely powdered ore, and 4 grams for a check analysis. Treat the ore in a porcelain-handled casserole, and extract it with 100 c.c. of conc. HNO_3 for a half hour, just below boiling, with frequent stirring. Then remove the cover and evaporate to dryness. In the same manner extract this residue with 50 c.c. of conc. HCl, heating with the cover on until all red fumes are gone. Now remove the cover, and evaporate low. Add 50 c.c. of 1 : 1 sulphuric acid and evaporate to heavy white fumes to remove the HCl. Cool. Add 50 c.c. of water; stir, heat, cool; filter off the insoluble residue and wash it with dilute sulphuric acid water. Dilute the filtrate and washings to 200 c.c., boil with permanganate and finish the determination as given on page 14.

(B) If the chemist wishes to reassure himself that even the last traces of vanadium have been extracted from the ore, he can burn off the insoluble residue obtained above in an iron crucible and fuse with 10 grams of peroxide of sodium. The fusion is kept *just* molten for two minutes. The melt is then dissolved out in the manner described on page 184 under Chromium in Chrome Ore. The sulphuric acid solution is filtered from any iron scales and the filtrate and washings are then analyzed for vanadium as above, and any vanadium found is added to that gotten in the main solution.

It is well for the operator to put a known amount of vanadium through all of the operations described in (A) to get the vanadium value of the standards for this method. Ferro-vanadium of known vanadium content is decidedly the best for the manipulation under (A). For (B) vanadic acid (V_2O_5) of known purity is much the best source of V.

Almost any ore of vanadium can be accurately assayed for vanadium by the combination of (A) and (B). The sulphide ore of vanadium (Patronite) should first have the sulphur roasted out of it at a low heat, when it can be analyzed according to (A) and (B) or the ash can be fused according to (B) alone.

ANALYSIS OF PITCHBLENDE FROM JOACHIMTHAL, AUSTRIA

Uranium.—0.50 gram of the finely powdered mineral was dissolved in 30 c.c. of 1.20 nitric acid, heating until nothing but a white residue remained; took dry; acidulated with 100 c.c. of 1.20 hydrochloric acid, heating until all but silica was dissolved. Filtered; washed; took filtrate and washings again dry; took up as before; filtered; washed; ignited; weighed and finished for silica. The two filtrates and washings from the silica were combined and precipitated with ammonia for iron and alumina; the iron and alumina were filtered out; redissolved; washed; and the filtrate and washings were finished as in clay (see pages 408-409) for iron and alumina. The filtrates and washings from the two precipitations of the iron and alumina were blue, due to the presence of copper. The lime and magnesia in these filtrates were obtained therefrom as given on pages 409-410.

The ammonia precipitate of the iron and alumina contains all of the uranium also. This precipitate was analyzed for iron, alumina, uranium, and vanadium by the methods described on pages 353 to 362.

The copper was found on a separate portion after dissolving the ore as described and passing H_2S through the very slightly acid solution until it is thoroughly saturated in hot solution. The copper sulphide was dissolved by warming it in 1.20 nitric acid until all black substance was dissolved. The solution was then evaporated to thick fumes and the lead was filtered out as sulphide; washed and finished as described for lead in tungsten ores (see page 105). The copper in the filtrate from the lead was finished by cyanide titration as given on pages 205 to 207.

CHAPTER XIII

PART II

THE DETERMINATION OF VANADIUM IN SANDSTONES CONTAINING CARNOTITE, ROSCOELITE, AND CALCIUM VANADATE, ETC.

(A) IF the sandstone contains about 3 per cent V then take 3 grams of the finely powdered ore, and 4 grams for a check analysis. Treat the ore in a porcelain-handled casserole, and extract it with 100 c.c. of conc. HNO_3 for a half hour, just below boiling, with frequent stirring. Then remove the cover and evaporate to dryness. In the same manner extract this residue with 50 c.c. of conc. HCl, heating with the cover on until all red fumes are gone. Now remove the cover, and evaporate low. Add 50 c.c. of 1 : 1 sulphuric acid and evaporate to heavy white fumes to remove the HCl. Cool. Add 50 c.c. of water; stir, heat, cool; filter off the insoluble residue and wash it with dilute sulphuric acid water. Dilute the filtrate and washings to 200 c.c., boil with permanganate and finish the determination as given on page 14.

(B) If the chemist wishes to reassure himself that even the last traces of vanadium have been extracted from the ore, he can burn off the insoluble residue obtained above in an iron crucible and fuse with 10 grams of peroxide of sodium. The fusion is kept *just* molten for two minutes. The melt is then dissolved out in the manner described on page 184 under Chromium in Chrome Ore. The sulphuric acid solution is filtered from any iron scales and the filtrate and washings are then analyzed for vanadium as above, and any vanadium found is added to that gotten in the main solution.

It is well for the operator to put a known amount of vanadium through all of the operations described in (A) to get the vana-

CHAPTER XIV

PART I

QUALITATIVE AND QUANTITATIVE TESTS FOR COBALT AND NICKEL IN STEEL AND METALLIC COBALT

DISSOLVE 0.500 gram of drillings in a mixture of 30 c.c. 1.20 HCl and 30 c.c. of conc. nitric acid. Heat until the insoluble residue is bright yellow if tungsten is present. Filter on a double 11 cm. filter; wash free of iron with 1 : 10 HCl. Make one basic acetate separation as in the gravimetric method; filter, wash a few times with acetate wash. Evaporate the filtrate and washings, if necessary, to 200 c.c. Now warm the solution with a drop or two of ammonia to see if any small amount of iron separates out. Filter again, as iron interferes with cobalt test, and wash a few times with ammonia wash; add an excess of dimethylglyoxime to the ammoniacal filtrate. If only a brown coloration results that does not turn to a scarlet precipitate, then cobalt is present. If a scarlet precipitate forms at once or in a few minutes then nickel is present (see Brunck's method for nickel).

If on filtering off this scarlet precipitate, after one hour's wait the filtrate is brown in color, then cobalt is also present. 0.25 per cent of cobalt in 0.500 gram of steel gives a very distinct brown color. The author would suggest this for a color method for small amounts of cobalt. If only a slight brown coloration forms on adding the "dimethyl" then several hours should elapse before making a decision, as a small amount of nickel, at first, gives only a brown coloration which eventually changes to a small scarlet precipitate.

If a per cent or two of cobalt is present then the acetate filtrates will show a pink coloration which is in itself a sure proof of the presence of cobalt; i.e., before any "dimethyl" is added. This pink color looks exactly like a weak solution of $KMnO_4$.

QUALITATIVE TEST FOR COBALT IN STEEL IN THE PRESENCE OF NICKEL, IRON, CHROME, ETC.

Dissolve 1 gram in nitric acid or in the before mentioned mixture of nitric and hydrochloric acid; boil down to 20 c.c.; add an excess of ammonia. Redissolve in glacial acetic acid; add a large excess of potassium nitrite and in a little time a yellow precipitate of potassium cobaltic-cyanide will separate out, and look very much like the yellow precipitate obtained with molybdate solution, in phosphorus analysis.

To prevent frothing add some alcohol immediately after putting in the potassium nitrite.

Gravimetric Method for Cobalt.—*In steels either in presence or absence of tungsten, molybdenum, vanadium, and chromium.*

Weigh 1 gram and 500 mgs. of sample and transfer to No. 5 porcelain dishes. Dissolve each in a mixture of 30 c.c. conc. HCl and 30 c.c. conc. HNO_3. When frothing is over, place over moderate flames on graphite baths and heat for about one hour, or until residue in dish is of a clean bright yellow color. Rinse off cover glasses and sides of dishes with water, then add 100 c.c. conc. HNO_3 and take to dryness, lowering flames to avoid loss from spurting when contents of dishes are nearly dry. (This is conveniently accomplished overnight.)

Bake over a bare flame or much better in an electric muffle furnace (see page 119) until nitric fumes are driven off. When sufficiently cool to prevent cracking the dishes, add 40 c.c. conc. HCl, and with cover glass on, digest for thirty minutes, or until all soluble constituents are in solution; boil to volumes of about 25 c.c.; dilute with water to about 100 c.c.; and evaporate to about 75 c.c.

Rinse off cover glasses into dishes, add pulp, filter on double 11 cm. filters into 600 c.c. beakers. Wash precipitate, until free of iron, with a 1 : 10 HCl wash. Set aside filtrate which contains the bulk of the cobalt.

Treatment of the Precipitate.—Burn off in clean platinum crucibles to yellow powder, using nickel wire to break up hard particles. Weigh when cool, add 2 or 3 drops H_2SO_4 and 10 c.c. hydrofluoric acid and drive off the SiF_4 in a moderately warm muffle. When dry remove any outside dirt from crucible with damp cheese-cloth, drive off SO_3 fumes with aid of a Bunsen or Chaddock burner flame, heating finally to redness; cool, weigh. Loss in weight represents SiO_2, which, multiplied by 49.63, gives silicon. Calculate to percentage.

To contents of each crucible add 8 grams Na_2CO_3. Fuse with lids on for fifteen or twenty minutes. Let cool slightly and extract the melts with hot water in platinum dishes. When salts are in solution, which should not require more than ten minutes heating, remove the crucibles and rinse them thoroughly with water into dishes so that they contain no carbonate. Filter on double No. 9 cm. filters. Discard this filtrate. Wash precipitate with water until free of alkali to phenolphthalein. Burn off in same crucibles in which fusions were made. Weigh when cool.

Differences in weight between the final silicon-free weight and this one represents WO_3, which, when multiplied by 0.7931, gives tungsten. To the final residue in the crucible is added 10 c.c. conc. HCl and the crucible is heated gently until contents are dissolved.

Transfer dissolved content of each crucible to its respective beaker which contains the main cobalt filtrate. Total cobalt is now in 600 c.c. beakers.

Nearly neutralize with ammonia. Dilute to about 400 c.c. with water. Heat to 80° C. and pass H_2S through for twenty minutes or until precipitate separates out distinctly. Remove and let settle for at least one-half hour. Filter on double 11 cm. filters into 600 c.c. beakers, washing precipitate with H_2S wash (2 drops 1 : 1 HCl, 500 c.c. water, saturated with H_2S).

Precipitate contains MoS_3 and other metals that are precipitated in acid solution. Ignite the sulphides at a low reddest heat in porcelain; weigh; extract with ammonia and filter; wash with filtered ammonia water and again weigh. Loss in weight is MoO_3, of which $66\frac{2}{3}$ per cent is molybdenum.

Filtrate from Sulphides.—Concentrate to about 50 c.c., add 50 c.c. conc. HCl, then 1 gram $KClO_3$ and concentrate to 30 c.c., keeping covered until all fumes of chloric acid are gone to prevent loss by spraying. Dilute to 150 c.c., add 50 c.c. conc. HCl, and evaporate to 50 c.c. volume, to remove, entirely, the free chlorine. Finally, dilute to 300 c.c. with water, add ammonia until a faint cloud forms that will not stir out. Then add 20 c.c.

and 10 c.c. of ammonium acetate to the 1 gram and 500 mgs. weights respectively. (2 c.c. = 1 gram ammonium acetate.)*

Put on Argand burner stove and allow them to boil for about two minutes. Remove from fire; allow acetates to settle; filter through double 15 cm. filters into 600 c.c. beakers that have been previously boiled out with dilute HCl. Wash precipitate fifteen or twenty times with acetate wash. Set aside filtrates. Dissolve precipitate in 50 c.c. HCl (1 : 1) by heating and pouring back and forth several times, then washing filter free of iron with 1 : 10 HCl wash. Make a second basic acetate separation. using 15 c.c. and 8 c.c. of ammonium acetate respectively for the 1 gram and 500 mgs. weights. Filter into 600 c.c. beakers and wash as before.

The Combined Acetate Filtrates.—If these filtrates contain much cobalt they will be pink. Heat to boiling; make faintly ammoniacal; add 5 c.c. of 1 : 1 ammonia in excess and last of all 50 c.c. saturated solution of microcosmic salt. Stir vigorously, otherwise bumping may break beakers. A blue precipitate forms which continuous stirring changes to a crystalline grape-colored precipitate that settles rapidly, leaving a water-white supernatant liquid. Filter on 11 cm. filters into clean liter beakers, washing precipitates with water containing 4 c.c. ammonium acetate, until free of chlorides, testing a few drops of the acidulated washings with silver nitrate solution. Burn off precipitates in weighed platinum crucibles over low flame at first, then increase to bright red heat; break up lumps with a nichrome or platinum rod. Cool, and weigh as cobalt, nickel, and manganese pyrophosphates and a little SiO_2 (C). Determine manganese in a separate portion by sodium arsenite titration, calculate to $Mn_2P_2O_7$ and deduct. Dissolve contents of crucibles with (1 : 1) HCl; filter; wash with 1 : 10 HCl, then with water; burn and weigh small amount of silica and deduct from (C). The remainder is $Co_2P_2O_7$, of which 40.39 per cent is Co.

The filtrates and washings from the phosphates of Co, Ni, and Mn usually contain a little Co and most of the Ni, etc., which are removed by saturation with H_2S in hot solution as follows: Heat the latter to 70° or 80° C., pass H_2S through for about thirty minutes. Black CoS and NiS are precipitated. Filter on double 11 cm. filters and wash about fifty times or until free of salts with water containing 2 grams ammonium acetate and saturated with H_2S. Burn off and weigh as CoO, of which 78.66 per cent is Co. Add this cobalt to that found from phosphate precipitation to get total cobalt. Deduct the Ni found on a separate portion.

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* Use an ammonium acetate solution that has been made neutral, or very faintly alkaline with ammonia.

The gravimetric method for cobalt powders and ferro-cobalt is the same as in Co steels except that but 0.5 gram is taken for the Co determination.

VOLUMETRIC METHOD FOR COBALT IN STEEL
(PRELIMINARY REMARKS)

Cobalt cannot be titrated quantitatively with KCN, exactly, as nickel owing to interfering reactions that take place. If the attempt is made to titrate cobalt *alone* with cyanide and silver a black precipitate forms that obscures the end-point. This is due to the formation of silver cobaltic-oxide.

The author, after several months of experimenting, found that by the use of tartaric acid and by always having not less than 1 gram of iron in solution per 0.1 gram of Co and by strict adherence to the following details, titrations, even up to 100 mgs. of cobalt, can be made with accuracy. Dissolve 0.8 gram and 1.0 gram of the steel in 40 c.c. of 1 : 3 sulphuric acid; add 15 c.c. of 1.20 nitric acid and digest the steel, if tungsten be present, until the latter is bright yellow; cool; add 12 grams of tartaric acid; dilute to 100 c.c.; add 90 c.c. of 1 : 1 ammonia; drop in a piece of litmus paper and then drop in 1 : 3 sulphuric acid from a burette with great care, until the litmus paper just turns from a blue to a red; then add exactly 4 c.c. of 1 : 1 ammonia in excess and no more, before titration with KCN.

The author uses c.p. cobalt powder for standardizations. Its purity can be checked by the phosphate method as given for steels. Nickel in cobalt steels and metals is determined by Brunck's method.

It is extremely important to have the excess of ammonia in all tests and standardization mixtures as nearly alike as possible. Varying amounts of free ammonia cause discordant results, and 10 c.c. of ammonium acetate to the 1 gram and 500 mgs. weights respectively. (2 c.c. = 1 gram ammonium acetate.)*

Put on Argand burner stove and allow them to boil for about two minutes. Remove from fire; allow acetates to settle; filter through double 15 cm. filters into 600 c.c. beakers that have been previously boiled out with dilute HCl. Wash precipitate fifteen or twenty times with acetate wash. Set aside filtrates. Dissolve precipitate in 50 c.c. HCl (1 : 1) by heating and pouring back and forth several times, then washing filter free of iron with 1 : 10 HCl wash. Make a second basic acetate separation. using 15 c.c. and 8 c.c. of ammonium acetate respectively for the 1 gram and 500 mgs. weights. Filter into 600 c.c. beakers and wash as before.

The Combined Acetate Filtrates.—If these filtrates contain much cobalt they will be pink. Heat to boiling; make faintly ammoniacal; add 5 c.c. of 1 : 1 ammonia in excess and last of all 50 c.c. saturated solution of microcosmic salt. Stir vigorously, otherwise bumping may break beakers. A blue precipitate forms which continuous stirring changes to a crystalline grape-colored precipitate that settles rapidly, leaving a water-white supernatant liquid. Filter on 11 cm. filters into clean liter beakers, washing precipitates with water containing 4 c.c. ammonium acetate, until free of chlorides, testing a few drops of the acidulated washings with silver nitrate solution. Burn off precipitates in weighed platinum crucibles over low flame at first, then increase to bright red heat; break up lumps with a nichrome or platinum rod. Cool, and weigh as cobalt, nickel, and manganese pyrophosphates and a little SiO_2 (C). Determine manganese in a separate portion by sodium arsenite titration, calculate to $Mn_2P_2O_7$ and deduct. Dissolve contents of crucibles with (1 : 1) HCl; filter; wash with 1 : 10 HCl, then with water; burn and weigh small amount of silica and deduct from (C). The remainder is $Co_2P_2O_7$, of which 40.39 per cent is Co.

The filtrates and washings from the phosphates of Co, Ni, and Mn usually contain a little Co and most of the Ni, etc., which are removed by saturation with H_2S in hot solution as follows: Heat the latter to 70° or 80° C., pass H_2S through for

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* **Use an ammonium acetate solution that has been made neutral, or very faintly alkaline with ammonia.**

Add exactly 4 c.c. ammonia (1 : 1) to each neutral test solution before beginning to titrate. It is very important that the excess of ammonia be the same for standards and tests. (See Preliminary Remarks.)

Add 2 c.c. KI solution, then exactly 2 c.c. $AgNO_3$ solution, which produce quite a turbidity. Stir and add KCN solution rapidly at first and slowly toward the end until the cloud just disappears. Record time at that moment and let stand six minutes. Record readings of "Silver" and "Cyanide" burettes.

At the end of six minutes clear up the newly formed cloud, slowly, with cyanide and add the amount thus used to that already consumed. Titration is now finished. Disregard any subsequent clouds that are almost certain to form. Titration of 1 gram of a non-cobalt steel, to get the relation between cyanide and silver, is the next step and is as follows: After dropping in the 2 c.c. of KI (from small pipette or graduate) and 2 c.c. $AgNO_3$ from burette, clear up carefully and slowly with KCN solution and record readings. Since all steel contains at least a trace of copper or nickel, this titration is made in order to eliminate any interference from this cause. This having been done, add 10 c.c. KCN solution, then carefully bring on a faint cloud with $AgNO_3$ solution, just clearing with a drop or two of KCN to be sure of no appreciable excess. This titration gives the relative comparison of cyanide and silver solutions, showing that 1.1 c.c. of KCN equal 1.0 c.c. of $AgNO_3$.

The calculations are the same as in the similar method for nickel, page 227. Deduct any nickel found on a separate portion by Brunck's method or the modified form of it. It is quite unlikely that appreciable amounts of nickel will be found in cobalt steels. The same can be said of copper, although the latter can be removed beforehand by H_2S.

Standardizations and Calculations.—Determine the blank first. Add 2 c.c. KI solution, then 2 c.c. $AgNO_3$ solution. Add KCN solution, drop by drop, until white cloud of AgI disappears. Take burette readings for silver and cyanide solutions; then add a known amount of cyanide, about 10 c.c., and titrate to a faint cloud with silver nitrate. Calculate silver nitrate in terms of cyanide, e.g.,

$$11.1 \text{ c.c. KCN} = 10.1 \text{ c.c. } AgNO_3.$$

$$1 \text{ c.c. } AgNO_3 = 1.1 \text{ c.c. KCN.}$$

Standard mixtures:

(1) 30 mgs. C. P. cobalt and 800 mgs. high-speed steel.
(2) 50 mgs. C. P. cobalt and 1 gm. high-speed steel.
(3) 80 mgs. C. P. cobalt and 1 gm. high-speed steel.
(4) Blank, no cobalt added and 1 gm. high-speed steel.

Put the above mixtures through all of the foregoing operations until the point of titration; then add 2 c.c. KI solution, also exactly 2 c.c. $AgNO_3$; then with constant stirring drop in KCN solution until the cloud disappears. Record first and last readings of burettes. Note the time. Wait exactly six minutes, then read the KCN burette and clear up the second cloud cautiously. Take reading and add it to former KCN reading. Deduct (2.0×1.1) c.c. from the total KCN reading; the remainder represents KCN consumed by the cobalt.

EXAMPLE

0.050 gm. metallic cobalt used, which contains 97.21 per cent Co.

KCN to clear first cloud.	KCN to clear second cloud.	$AgNO_3$
0.0	71.2	14.0
69.9	73.9	16.0
69.9	2.7	2.0
2.7		×1.1
72.6		2.2
−2.2		

70.4 = 0.05 gm. × 0.972 gm. Co = 0.0486 gm. Co., or 1 c.c. KCN = 0.0006904 gm. cobalt

Titrate sample in exactly the same way as the standard mixtures. Since 800 mgs. weights have a general tendency to go lower than 1 gm. weights for reason stated in the introduction, use the higher factor on those weights, viz.:

30 mgs. standard + 800 mgs. steel
1 c.c. KCN = 0.000704 gm. cobalt

. . . .

50 mgs. standard + 1 gm. steel
1 c.c. KCN = 0.0006904 gm. cobalt

. . . .

800 mgs. sample required 49 4 c.c. KCN. Therefore the steel contained 49.4×0.000704 mg. Co or 0.03477 mg. Co. Hence per cent cobalt in sample equals 0.03477÷0.8×100, or 4.35 per cent cobalt.

1 gm. sample required 63.0 c.c. KCN. Therefore the steel contained 63.0×0.0006904 gm. Co, or 0.04349 gm. Co, or 4.35 per cent cobalt.

Nickel in Cobalt Steels

Weigh 1 gram and 0.9 gram of sample into 400 c.c. beakers. Dissolve in 25 c.c. H_2SO (1 : 3) over moderate flame. Oxidize with 10 c.c. HNO_3 (1 . 20); cool; add 5 grams citric acid per gram sample taken. Make slightly ammoniacal; dilute to 300 c.c.; add 20 c.c. of a 2 per cent alcoholic solution of dimethylglyoxime; let stand two hours; filter on double 11 cm. filters; wash about twenty-five times with dimethyl wash (10 c.c. of 2 per cent dimethyl to 500 c.c. water). Dissolve by passing 25 c.c. 1 . 20 HNO_3 (cold) back and forth on the filter. Wash about forty times with nitric wash (10 c.c. 1 . 20 HNO_3 to 500 c.c. water). Make filtrate ammoniacal and repeat dimethyl precipitation to remove cobalt which is carried out with nickel in considerable quantity. Filter and wash as above. The precipitate should be bulky and of a brick-red appearance. If not, make a third precipitation to insure complete removal of cobalt.*

Volume of dissolved precipitate should be about 100 c.c. Boil about ten minutes. Add 15 c.c. H_2SO_4 (1 : 3); cool; add 2 grams citric acid; make slightly ammoniacal, volume about 200 c.c.; titrate at ordinary room temperature in usual manner for nickel titration in plain nickel steel by the KCN method; calculate per cent nickel in sample.

When nickel is present along with cobalt in steels, run nickel standards in the same manner as described for cobalt standards, i.e., clearing up of first cloud after waiting six minutes. Per cent nickel having been determined by separate operation, calculate number of c.c. used for nickel by dividing amount of nickel found by the nickel value of the cyanide solution standardized as above; deduct from total KCN used by the cobalt plus nickel and calculate cobalt by multiplying the remaining c.c by the cobalt value of the solution.

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* A filtrate at this point, free from brown color, indicates the complete removal of the cobalt from the red nickel precipitate.

STANDARDIZATION OF KCN SOLUTION WITH NICKEL AMMONIUM SULPHATE, FOR COBALT NICKEL STEELS

200 mgs Ni. Am. Sulphate. 800 mgs High Speed Steel

KCN to clear first cloud.	KCN to clear second cloud	$AgNO_3$
19.3	58.0	48.0
51.6	58.4	50.0
———	———	———
32.3	0.4	2.0
.4		×1.1
———		———
32.7		2.2
2.2		
———		
30.5		

0.0146 gm. of Ni in 0.100 gram of Ni Am. sulphate

$0.0146\ \text{gm.} \times 2 \div 30.5 = 0.000957$, or

1 c.c. KCN solution equals 0.000957 gm nickel

340 mgs. Ni. Am. Sulphate. 1 gm. High Speed Steel.

KCN	KCN	$AgNO_3$
1.2	78.6	52.0
54.0	80.6	54.0
———	———	———
52.8	2.0	2.0
+2.0		
———		
54.8		
2.2		
———		
52.6		

$0.0146 \times 3.4 \div 52.6$ equals 0.0009437, or

1 c.c. KCN solution equals 0.0009437 gm. nickel.

CALCULATIONS FOR COBALT IN COBALT NICKEL STEELS

Sample 800 mgs.

$AgNO_3$	1st titration. KCN	2d titration. KCN required to clear second cloud which formed after six minutes
54.0	0.2	1.0
56.0	78.4	5.7
———	———	———
2.0	78.2	4.7
	4.7	
	———	
	82.9	
	2.2	
	———	
	80.7	
	27.45	
	———	
	53.25	

Cobalt and nickel required 80.7 c.c. KCN in 0.8 gram of sample. Since 3.26 per cent nickel was found by separate determination, therefore 0.0326 × 0.8 = 0.02608 gram nickel, which divided by 0.00095 = 27.45, or 27.45 c.c. of KCN to be deducted from the total, or 80.7 c.c. This gives 80.7 − 27.45, or 53.25 c.c. of KCN used by cobalt alone. 53.25 × 0.00068 × 100 ÷ 0.8 = 4.52 per cent Co.

	Sample 1 gm.	
	1st titration.	2d titration.
$AgNO_3$	KCN	KCN required to clear the second cloud which forms after six minutes
56.0	0.6	57.0
58.0	99.0	62.2
2.0	98.4	5.2
	5.2	
	103.4	
	2.2	
	101.2	
	34.3	
	66.9	

Cobalt and nickel required 101.2 c.c. of KCN for 1 gm. sample. Since 3.26 per cent nickel was found by separate determination, therefore 0.0326 × 1.0 ÷ 0.00095 = 34.31. 101.2 − 34.3 = 66.9 or KCN used by cobalt alone. 66.9 × 0.00068 ÷ 1 × 100 = 4.55 per cent cobalt.

THE DETERMINATION OF SMALL AMOUNTS OF NICKEL IN THE PRESENCE OF LARGE PER CENTS OF COBALT

Dissolve 1 or more grams of the cobalt in 40 c.c. of 1.20 nitric acid; add 15 c.c. of 1 : 3 H_2SO_4; boil off nitrous fumes; cool; add 5 grams of citric acid per gram of cobalt taken; add a slight excess of ammonia. Cool and add 20 c.c. of a 2 per cent solution of the dimethylglyoxime in 95 per cent alcohol for every gram of metallic *cobalt* present. Let the cold solution stand for at least one hour; filter out the precipitate of the nickel compound which owing to contamination with Co may not have its true scarlet color. It is washed with "dimethyl" wash consisting of 10 c.c. of the dimethyl solution diluted with 500 c.c. of water, and is redissolved in 25 c.c. of 1.20 nitric acid, and reprecipitated as before. The now scarlet precipitate is washed as at first; dissolved; 15 c.c. of 1 : 3 sulphuric acid are added to the solution which is then boiled fifteen minutes. Five grams of citric acid are added and the nickel is titrated with cyanide and "silver" as in steels. This method should also answer for the separation of small amounts of nickel from large amounts of elements, like manganese and chromium, which give very dark fluids when held in ammoniacal solution by ammonium citrate. In this way large weights of these elements could be taken as in the case of the Co.

THE TESTING OF NICKEL FOR SMALL AMOUNTS OF COBALT

Dissolve 4 or 5 grams of the nickel millings in 1.20 nitric acid, using 10 c.c. of the acid for every gram of the sample taken. Boil off the red fumes; dilute to 20 c.c.; add ammonia until a slight precipitate forms that does not dissolve on long stirring, if iron or aluminum be present; if neither of these elements are in the solution then add the ammonia until a piece of litmus paper floating in the solution just turns blue. Now add acetic acid (1 part of glacial acetic acid diluted with an equal volume of water) until the precipitate just dissolves, or the litmus turns to red, or the solution smells of a slight excess of acetic acid; add an excess of 10 c.c. of the acetic acid; dilute the solution to 400 c.c. and add 25 grams of potassium nitrite when, after a few minutes, the solution will begin to cloud with a precipitate of the tri-potassium cobaltic nitrite. If the percentage of Co present is very small, being less than 0.1 per cent, then the precipitate will appear yellow only after the lapse of an hour or two. If there be from 0.3 to 0.5 per cent of Co in the sample then the cobalt will quickly form in a bright yellow powder, and slowly settle to the bottom of the beaker. After standing twelve hours the precipitate is filtered off and washed with 25 grams of potassium nitrite dissolved in 300 c.c. of water and made slightly acid with acetic acid. The precipitate should be mixed with some finely divided filter pulp before filtering. Wash it until the washings no longer give any color with a solution of dimethylglyoxime.

The yellow precipitate is then dissolved in 40 c.c. of hot 1 : 1 HNO_3 and the filter is thoroughly washed with the acid. The filtrate and washings are made slightly ammoniacal and 20 c.c. of "dimethyl" are added to each test. This gives a brown color whose depth is proportional to the cobalt present and is compared with known amounts of cobalt ammonium sulphate put through all of the above operations. The color is almost exactly the same shade as that obtained in the color carbon test in steels.

If, when the yellow cobalt precipitate is washed with the above nitrite wash, it is found that the nickel is very difficult to remove, the yellow precipitate can be redissolved, reprecipitated, and washed again. This treatment should remove the nickel to the extent that the cobaltic-nitrite can be readily washed free of nickel test with the "dimethyl" wash.

The above procedure constitutes a very delicate qualitative test for cobalt in the presence of nickel. Less than 0.100 per cent of Co can be readily detected in 5 grams of nickel. The operator should be careful to carry out either the qualitative or the quantitative precipitation exactly, as described for the quantitative method, as there are conditions which cause the cobalt to precipitate very slowly and imperfectly. If, when the nitric acid solution of the yellow precipitate is made ammoniacal, prior to the addition of the "dimethyl" to obtain the brown color, a precipitate of iron appears, this iron must be removed as iron also gives a color with this reagent. Make a basic acetate separation of the iron, in the usual way, in a volume of 100 c.c. Make a second basic acetate separation of the iron and combine the two filtrates and washings from the basic acetate precipitations; make ammoniacal; add the "dimethyl" and compare with the standard similarly treated, consisting of 0.2 gram of cobalt ammonium sulphate put through all of the above operations.

ANALYSIS FOUND

	Per Cent		Per Cent
Cobalt	0 600	Silicon	0 28
Nickel	98 400	Manganese	Trace
Iron	0 60	Copper	0.12

ELECTROLYTIC METHOD FOR COBALT AND NICKEL IN FERRO-COBALT AND IN COBALT POWDER

The following method is used by one large European concern for the valuation of their product: 20 grams are dissolved in moderately conc. nitric acid. Any insoluble matter is fused with $KHSO_4$ and the fusion is dissolved in diluted H_2SO_4 (1 : 3), added to the main solution and then all is transferred to a liter volumetric flask, diluted to mark and mixed well by repeatedly inverting the flask; 25 c.c. of this solution are accurately measured from a 50 c.c. burette that has been rinsed three times with some of the liter solution. These 25 c.c. are evaporated to thick fumes with H_2SO_4; diluted to 350 c.c. with water; and the copper is precipitated with H_2S. The Cu_2S is filtered out and washed with H_2S water containing a drop of H_2SO_4 in 500 c.c. The filtrate and washings from the Cu_2S are evaporated low, in a casserole; 5 c.c. conc. HNO_3 are added and 75 c.c. of conc. HCl; heated with lid on until all red fumes are gone; the lid is removed and evaporation to 10 c.c. follows. Dilute to 350 c.c.; make a double basic acetate separation of the iron as in gravimetric method; add 2 c.c. of acetate per 100 mgs. of cobalt present; filter off any iron acetate, wash with acetate water. To filtrate and washings add 35 c.c. H_2SO_4 of 30° Bé. and evaporate to fumes; take up with water and add 2 grams of sodium sulphite, also about 40 c.c. of ammonia of about 0.96 sp. gr. The strongly ammoniacal solution should now be about 100 c.c. volume. Electrolyze this solution in the cold with a current of 0.3 to 0.4 amp. and 6 volts for about six hours, using a platinum spiral and a gauze electrode of platinum. Weigh as cobalt plus nickel.

DETERMINATION OF THE NICKEL

One hundred c.c. of the liter solution are neutralized with KOH and KCN is added until the precipitate that forms is dissolved. Add an excess of KOH; add bromine water until a yellow color is obtained; and allow the precipitate to settle for one hour. The black precipitate of nickel oxide which still contains a little cobalt is filtered, washed with KOH water and redissolved in HCl containing bromine water. This Ni is then reprecipitated as before, redissolved and the solution is electrolyzed for nickel, as in the case of the Co. The nickel is then dissolved off the electrode with HNO_3. The nitric solution can be titrated with KCN.

Or precipitate the solution of the deposited nickel with a

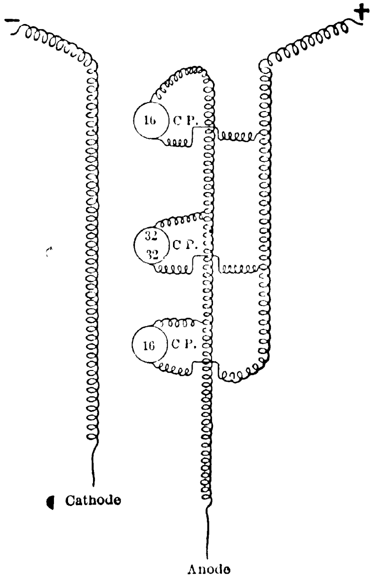
1 per cent alcoholic solution of dimethylglyoxime at 50° C. in excess of ammonia. Dry the precipitate to constant weight at 120°. The nickel is then deducted from the cobalt plus nickel determined from the 25 c.c. by electrolysis, and the cobalt obtained by difference.

THE METHOD GIVEN IN DETAIL FOR THE DETERMINATION OF COBALT AND NICKEL BY ELECTROLYSIS AS USED BY THE AUTHOR

For cobalt powder, cube or ferro-cobalt containing 70 per cent or more of Co, dissolve 0.2 gram (and 0.3 gram for a check) in 35 c.c. of 1 : 3 sulphuric acid, using 600 c.c. beakers. When the action is over, oxidize any iron by the addition of 10 c.c. of 1.20 nitric acid; boil down to 15 c.c.; add 50 c.c. of water and boil again to 15 c.c.; cool; make the basic acetate separation of the iron in the same way as described under ferro-manganese, page 244. Add 2 c.c. of the slightly ammoniacal ammonium acetate solution for each 100 mgs. of cobalt present. Filter out the acetate of iron; redissolve it and repeat the basic acetate separation. The combined filtrates from the two basic acetate separations are acidulated with 10 c.c. of H_2SO_4 and evaporated to 200 c.c. Ammonia is added until the solution takes on the faintest excess of ammonia. Then 100 c.c. more of 1 : 1 ammonia are dropped in and 2 grams of sodium sulphite. The solutions are transferred to 400 c.c. beakers and electrolyzed with a current of 0.45 ampere and 3.2 volts until the pinkish solution is entirely colorless. The electrolysis is conducted in pairs. The current is turned on and allowed to run all night.

The beakers are arranged so that they can be *lowered* away from the electrodes when the deposition of the cobalt is completed. The electrodes are rinsed off with distilled water; and another beaker is slipped under them and raised and lowered with the electrodes dipping in the water; a second and third beaker of water are also used to wash the electrodes as many more times. The cathode is then dried in an air bath at 100° C. for forty-five minutes; cooled; and weighed. It is again washed; dried; cooled; and weighed. The final weight less the weight of the cathode, taken before the analysis, equals the weight of the cobalt, and any nickel present. The author has found nickel from traces to 3 per cent in every case thus far, of cobalt of commerce.

Fig. 32 shows an arrangement of electric lamps whereby the amperage can be varied from 0.225 to 0.9 ampere, and from which, with a 220-volt circuit, an electromotive force of 3.2 volts can be obtained. At the points marked 16 c.p., 16 candle-power lamps are placed in the circuit. A 32-c. p. lamp is put in the socket so marked. With one 16-c.p. lamp burning



Sketch No. 32.

the current is 0.225 ampere; with two such in action the amperage is 0.45 and so on. With the 32-c. p. lamp the current is 0.45. With all three lamps the amperage is the sum total, or 0.9. The voltage on the main is 220. This group of lights can be arranged on a board 8 by 10 inches. One such group is of course needed for each determination. To determine which is anode and which is cathode, close the switch, wet a piece of turmeric paper and touch the ends marked "anode" and "cathode" to the paper, when the end which is cathode, or negative, will stain the turmeric red.

The solution from which the Co and Ni have been deposited, is saturated with H_2S, and any small amount of black sulphide that separates out is filtered out; washed with H_2S water; ignited in a porcelain crucible at a low red heat; weighed as CoO; multiplied by the factor 0.7866 to convert it to the equivalent of metallic Co; and added to the total of Co plus nickel found on the cathode. The cathode is then placed in hydrochloric acid, which quickly dissolves off the Co and Ni. The cathode is removed and rinsed thoroughly. To the solution and rinsings are added the solution of the small amount of the oxide which has meanwhile been dissolved in a little aqua regia. Make the total solution ammoniacal and precipitate the nickel out of the hot solution with 20 c.c. of the 2 per cent solution of dimethylglyoxime in alcohol. The red precipitate is dissolved in nitric acid; reprecipitated as before; washed with dilute nitric acid water; and finished by the ordinary titration with KCN and silver nitrate. The milligrams of metallic nickel so found are deducted from the total of Co and Ni found by the electrolysis plus any recovered by H_2S, giving the cobalt by difference. If the operator wishes to guard against the presence of copper, H_2S should be passed through the solution of the total cobalt plus nickel before adding the dimethyl. Any sulphides so precipitated are filtered out; washed and titrated with KCN for copper as in steels. The filtrate and washings from the copper are evaporated low; oxidized with nitric acid; and then the nickel is obtained with the dimethyl, as described. If the operator wishes, the nickel can be gotten on a separate portion as described under the determination of nickel in metallic cobalt.

The cylindrical cathode and disc anode of platinum are the most convenient form of electrodes for this work. One can use also a platinum dish for the cathode, suspending in the fluid in the dish any convenient form of platinum anode.

Phosphorus, *sulphur*, and *silicon* can be determined in metallic cobalt as in plain carbon steels. In all of the samples that the author has analyzed, at least, very accurate results for sulphur were obtained by the ordinary evolution method. These results were checked by gravimetric results obtained by the same method as recommended for sulphur in tungsten powder by fusing with a mixture of sodium carbonate and sodium peroxide. (See page 80.) The method given on page 122 should give accurate results.

MANGANESE IN HIGH PERCENTAGE COBALT STEEL AND METALLIC COBALT

Dissolve 0.100 and 0.05 gram of steel, cobalt powder, or ferro-cobalt in 20 c.c. of conc. HCl diluted with 10 c.c. water. Dilute to 50 c.c. and neutralize with ammonia. Redissolve the hydroxides in glacial acetic acid. Avoid much excess of acetic acid. Dilute to 100 c.c. with water and pass H_2S in the cold to remove the main portion of the cobalt. Filter off cobalt sulphide, wash it fifty times with H_2S water, evaporate filtrate and washings in a casserole to 20 c.c.; cool; add 100 c.c. conc. nitric acid; heat with cover on until all red fumes are gone; remove cover and evaporate to 25 c.c. Dilute to 50 c.c. with water and evaporate again to 25 c.c. Transfer to 10×1 inch test tubes and finish as in plain carbon steel. The bulk of the cobalt is removed only because it gives such a strong pink in nitric solution that the operator cannot get an end-point when titrating with arsenious acid as in steels. Steels containing 5 per cent Co do not interfere in this way, but if the percentage of Co runs much higher, the cobalt must be removed before titration.

Cobalt steels containing much chromium and tungsten should be dissolved in 20 c.c. of 1 : 3 H_2SO_4 and oxidized with 15 c.c. 1 : 20 nitric acid; boil down to 10 c.c.; filter off tungsten; wash with dilute H_2SO_4; neutralize with ammonia; acidulate with acetic acid and proceed as above. This removal of cobalt is only necessary in very high percentages, at least 10 per cent cobalt.

ANALYSES OF METALLIC COBALT AND FERRO-COBALT

	Per Cent Co	Per Cent Ni	Per Cent Fe	Per Cent Al	Per Cent Si	Per Cent S	Per Cent Mn	Per Cent P
Bar cobalt . .	94.40	2.59	1.25	1.17	0.31	0.031	0.21	0.016
Lump cobalt . . .	98.56	0.80	0.48	....	0.30	0.017	0.20	0.017
Powder	96.61	1.87	0.70	. . .	0.26	0.157	0.26	0.012
Cubes....	97.56	2.10	0.35	.	0.08	0.022	0.08	0.022
Ferro-cobalt.....	75.25	0.60	21.49	1.90	0.77	0.014	0.08	0.019

When neutralizing with ammonia, prior to adding the excess of acetic acid, do not completely precipitate the iron, etc., but just add enough ammonia to produce a slight permanent precipitate. Then redissolve the latter in acetic acid as directed.

Stellite.—Cobalt, Molybdenum, Iron, Manganese, Chromium.

Dissolve 1 gram and 800 mgs. in 30 c.c. conc. HCl and 30 c.c. conc. nitric acid; evaporate to 20 c.c.; add 100 c.c. conc. nitric acid and evaporate to dryness, but do not ignite, as cobalt may become insoluble. Dissolve in 50 c.c. conc. HCl; evaporate to 20 c.c.; transfer to 1000 c.c. boiling flask; and dilute to 200 c.c. Peroxidize; add Na_2O_2 until black precipitate forms and tends to settle; add 10 grams more of peroxide and 10 grams Na_2CO_3; bring just to boil; continue to boil ten minutes; cool; filter on double 15 cm. papers and wash with peroxide water.

Redissolve the black precipitate in 60 c.c. 1 : 1 HCl; and peroxidize again as before and so on until filtrates are free of yellow color. Three peroxidations are sufficient. Residue on filter is cobalt and iron. Dissolve off filter as before; filters are washed. Ash the filters and extract any remaining cobalt with 10 c.c. HCl and add to main cobalt and iron solution. Two basic acetate separations are made of this solution as in cobalt steel. Then finish filtrates by phosphate precipitation as in cobalt steels. The acetate of iron on the filter can be dissolved in HCl, reprecipitated and weighed; or titrated as in iron ore.

Chromium is obtained as in chromium ore, except that the iron and cobalt are filtered out and washed with sodium peroxide wash. Filtrate and washings are boiled for twenty minutes to remove H_2O_2 and titrated with ferrous ammonium sulphate as in chrome ore.

Molybdenum is gotten from a separate portion, dissolving in the same mixture as in cobalt steel. The molybdenum is then precipitated as in steel with H_2S.

ANALYSIS OF STELLITE

	Per Cent		Per Cent
Cobalt	60.80	Iron	0.52
Molybdenum	24.10	Silicon	0.27
Chromium	13.20	Phosphorus	0.02
Manganese	0.55		

Manganese is determined as in cobalt steel, removing most of the cobalt with H_2S.

Silicon is found by fuming with sulphuric acid, as in chrome steel.

Oxygen and Salts (Sodium Chloride, etc.) in Metallic Cobalt

The oxygen is determined on the finely powdered sample as in tungsten (see page 81).

Salts other than cobalt salts are determined by extracting the finely divided sample by boiling it in distilled water in a platinum dish until the decanted extract no longer leaves a residue on evaporation. The extract is decanted through a filter. The combined extracts are dried at 120° C. and weighed. The extract is then dissolved in water and a little HCl, if necessary; made very faintly ammoniacal and saturated with H_2S. Any precipitate so obtained is filtered out; washed with H_2S water; ignited in a porcelain crucible; weighed; and deducted from the weight of the extract dried at 120° C. The following is an analysis of an alleged c.p. metallic cobalt powder; Co, 95.45 per cent; Si, 0.01 per cent; C, 0.25 per cent; chlorides, other than cobalt salts, 1.89 per cent; O, 1.72 per cent.

CHAPTER XV

PART I

THE DETERMINATION OF NITROGEN IN STEEL AND IRON

A NUMBER of English and American chemists prefer to determine the nitrogen in steel by dissolving it in 1 : 1 HCl. The nitrogen is supposed to exist in the steel as Fe_5N_2 or Fe_4N_2 and is converted into ammonia by evolved hydrogen. This ammonia then combines with the HCl to form ammonium chloride. This solution of iron chloride and ammonium chloride is poured into a flask of the style shown on page 332 but of 700 to 750 c.c. capacity. A double bored stopper is used in the flask. Through one hole is passed a long-stemmed separatory funnel whose tube just dips under the fluid in the flask when all of the solutions are in it. The other hole in the stopper is for a glass delivery tube, one end of which just passes through the stopper into the flask and the other end is connected with a glass condenser of the Liebig type. Before introducing the solution of the sample, 12 grams of NaOH in 250 c.c. of water are put in the flask; the latter is connected with the condenser; and about half of the water is distilled off to remove any nitrogen that may be in the NaOH before the actual determination of that in the sample is begun.

Having purified the NaOH from any nitrogen it may contain, as above, the 1 gram of sample, which has meanwhile been dissolved in 20 c.c. of 1 : 1 HCl is run slowly into the flask (which is first connected with the condenser) via the separatory funnel. When all of the solution of the steel is in the flask, it is given a whirling motion to mix thoroughly the HCl solution of the steel with the NaOH. The mixture is then brought to a boil, and the boiling is continued until the distillate which is received in Nessler tubes no longer gives the characteristic brown color with Nessler solution.* The total distillate is then treated with 2 c.c. of the Nessler reagent per each 200 c.c. of distillate. The brown-colored solution so obtained is then matched against standard ammonium chloride which is made by dissolving 0.0382 gram of this salt in one liter volume of water. As ammonium chloride contains 26.18 per cent of nitrogen, 0.0382×0.2618 equals 0.010 gram of nitrogen, hence 1 c.c. of the above standard is equivalent to 0.00001 gram of nitrogen.

The most convenient way to make this comparison is as follows: Suppose that 200 c.c. of the distillate were obtained. This would then be treated with 2 c.c. of the Nessler solution and well mixed in a Nessler tube or other convenient comparison tube. Then place 200 c.c. of water in a duplicate comparison tube together with 2 c.c. of the Nessler solution. Next drop from a burette, with constant mixing, into this Nessler solution and water, some of the standard ammonium chloride until the color of this mixture just matches that of the distillate. Suppose that the reading of the burette showed that it required an addition of 35 c.c. of the ammonium chloride standard to produce in the imitation mixture a depth of color equal to that of the distillate obtained from the steel; this gives the volume of the test as 202 c.c. and that of the standard as 237 c.c. As 35 c.c. of the standard solution of ammonium chloride were required then the distillate must contain 0.00035×202÷237×100÷1 or 0.029 per cent nitrogen. A blank determination must be run including all of the chemicals and operations, and any nitrogen so obtained must be deducted from that found in the steel. The accuracy of the manipulations can also be tested by putting a measured amount of the ammonium chloride standard solution through all of the operations, and any nitrogen found in excess of that added in the form of ammonium chloride should equal the blank determination.

Ledebur prefers to determine nitrogen in iron or steel by dissolving 10 grams of the sample in a flask similar to the one used in the foregoing method, using 120 c.c. of dilute sulphuric acid made by diluting 1 part of conc. sulphuric acid with 4 parts of water. When the sample is entirely dissolved, the flask *A*,

---

* The reaction causing the brown coloration is explained by the following equation:

$$2(2KI, HgI_2)+NH_3+3KOH=NHg_2IH_2O+7KI+2H_2O.$$

Fig. 33, is connected to a duplicate flask *E* containing a little water. This second flask is in turn connected with a nitrogen bulb *F* approximating very closely to the Volhard nitrogen bulb. The Volhard bulb has a stopper through which the delivery tube from flask *E* passes. This delivery tube dips almost to the bottom of the nitrogen bulb in which is placed exactly 25 c.c. of N/10 sulphuric acid. One hundred c.c. of water containing 40 grams of NaOH are poured through the separatory funnel into the solution of the steel in *A*. The mixture of hydroxide of iron and NaOH is boiled gently and at the same time a stream of air is drawn through the entire apparatus. The boiling and drawing of air is continued for an hour. By this time all of the ammonium sulphate formed from the nitrogen in the steel is supposed to have been converted into ammonia by the action of the NaOH and been drawn over into the N/10 sulphuric acid in the nitrogen bulb. The contents of the latter are then titrated with N/10 NaOH with a few drops of methyl orange for an indicator. The number of c.c. of the N/10 sulphuric acid found by this titration to have been neutralized by the ammonia coming from the nitrogen in the steel, is multiplied by the factor 0.001401 to find the part of a gram of nitrogen that existed in the 10 grams of steel. This method is to be commended by reason of the fact that a large sample can be taken, and it is not dependent on the operator's skill in matching colors.

Calculations.—The factor 1 c.c. of N/10 sulphuric acid equals 0.001401 gram of nitrogen is obtained as follows: Since 1 c.c. of N/10 sulphuric acid contains 0.0049038 gram of H_2SO_4, and this acid unites with ammonium hydroxide according to the equation $H_2SO_4+2NH_4OH=(NH_4)_2SO_4+2H_2O$, we have the proportion given below:

$$H_2SO_4 : 2N : : 1 \text{ c.c. } N/10\ H_2SO_4 : X$$

or

$$98.08 : 28.02 : : 0.0049038 : X$$

or

$$X=0.0014009 \text{ gram of nitrogen}$$

Suppose it is found by titration of the 25 c.c. of H_2SO_4, after the absorption of the ammonia formed from the nitrogen in the steel, that only 23 c.c. of the N/10 NaOH are required to discharge the pink color given to the 25 c.c. of the N/10 H_2SO_4 by the methyl orange. This would mean that 25 c.c. less 23 c.c. or 2 c.c. of the N/10 sulphuric acid had been neutralized by the ammonium hydroxide coming from the nitrogen in the steel and the blank. If there were no deduction for a blank then the percentage of nitrogen found would be 0.001401×2×100 divided by 10 or 0.028 per cent nitrogen.

Nessler Solution.—Thirty-five grams of potassium iodide are dissolved in 200 c.c. of distilled water. To this KI is added a saturated solution of mercuric chloride until a faint precipitate is obtained. Next add 160 grams of potassium hydroxide. Dilute to one liter and add more of the mercuric chloride solution until a small permanent precipitate of mercuric iodide forms and remains. This precipitate on settling should leave a pale yellow supernatant fluid which is supposed to become more sensitive with age. It gives a brownish yellow tint to small traces of ammonium or its salts in solution. If large quantities of ammonia are in solution the Nessler reagent produces a precipitate.

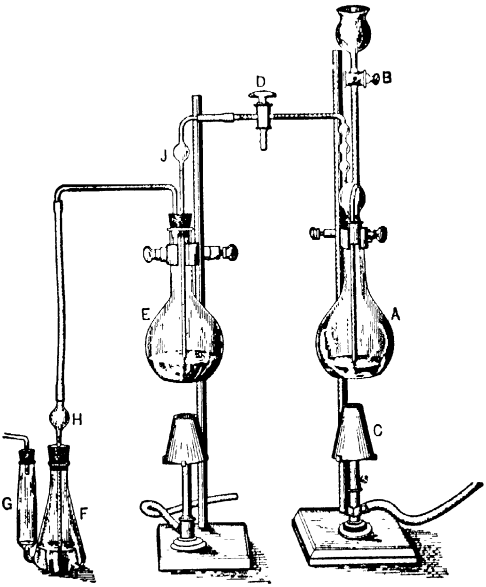


Fig. 33.

According to Braune when the nitrogen reaches 0.035 per cent in the high carbon steels it causes serious brittleness.

It is very necessary in making nitrogen determinations to carry out the work in a room free from all ammonia fumes. The work should be done in a place apart from the other laboratory work. In drawing air through the train in the method described by Ledebur it would seem advisable to purify such air by passing it through a wash bottle containing some dilute sulphuric acid, before it enters the boiling flask.

APPARATUS OF LEDEBUR FOR THE DETERMINATION OF NITROGEN IN STEEL

In his Leitfaden für Eisenhütten-Laboratorien, Ledebur uses the apparatus shown in Fig. 33. The steel is dissolved in *A* and the NaOH is introduced through *B*. The air is drawn through *A* and *E*, carrying the ammonia formed from the nitrogen in the steel through *E* over into the measured amount of N/10 sulphuric acid in *F* where it is absorbed and determined as already described.

CHAPTER XVI

THE ANALYSIS OF GRAPHITE AND GRAPHITE CRUCIBLES

THE total carbon is determined by direct combustion in the electric furnace. The sample is reduced to sufficient fineness to pass through No. 11 bolting cloth. A hardened steel mortar is used with a ball pestle. The chamber of the mortar is 3½ inches deep by 1¾ inches in diameter. The total thickness of the steel block is 4 inches. The pestle fits, exactly, the bottom of the mortar. The material is pounded into this opening by striking on the end of the pestle with a hammer. It is then taken out and ground in an agate mortar to loosen the mass which is sifted through the bolting cloth. The portion that does not pass the cloth is put back into the steel mortar and hammered again, and so on until the sample all passes through the cloth.

0.200 to 0.300 gram of sample is used, and it burns completely in oxygen in the electric furnace. Forty-five minutes elapse from the time the sample is put in the furnace until the absorption apparatus is detached for the final weighing of the carbon dioxide formed. The weight of the CO_2 multiplied by 27.27 and divided by the weight taken for analysis yields the exact carbon in the sample.

VOLATILE MATTER

One gram of sample is burned in a platinum crucible with a *slow* stream of oxygen passing in through a hole in the lid of the same. The lid is removed and the contents stirred with a nickel wire at intervals of about twenty minutes. The porcelain tube of a Rose crucible is used to conduct the oxygen through the hole in the platinum lid. When the contents of the crucible no longer lose weight the ignition is stopped. The total loss of weight less the weight of carbon by combustion equals the volatile matter other than carbon, such as water and sulphur.

A direct determination of water can also be made by igniting the substance in a stream of air, dried by passing it through a jar of phosphoric anhydride such as is used in the carbon combustion train. (See Fig. 7 (*J*), page 265.) The sample is put in a clay boat and heated to redness in a porcelain or quartz combustion tube.* In the outlet end of the tube is attached, by means of a rubber stopper and glass tube, an absorption jar or U-tube, see *B*, Fig. 1, page 85, containing phosphoric acid. The outlet of the absorption jar is guarded against the ingress of moisture by a calcium chloride tube closely filled with bits of stick caustic potash. The air is drawn through by a suction pump. At intervals of twenty minutes the heat is lowered, the passing of the air is stopped and the absorption jar is weighed. It is attached again, the heat raised to redness for another twenty minutes, and the weighing is again made as before, and so on until there is no more gain than is obtained by a blank test carried through in the same manner. The total increase in weight of the phosphoric anhydride less the blank is calculated to percentage as water.

A blast lamp flame, or an electric muffle (see page 120), is used to expel the carbon, obtain the ignition loss, and the ash for analysis. The ash from the 1 gram taken for ignition loss is analyzed for its various constituents exactly as a clay. It is fused with a mixture of 10 grams of anhydrous carbonate of soda plus one gram of niter in a platinum crucible. The melt is dissolved out with water in a platinum dish, using heat to hasten the solution. The water extraction is transferred to a No. 6 porcelain dish. The dish is covered with a watch glass, and 1 : 3 sulphuric acid is allowed to flow down the under side of the lid until 125 c.c. in all have been slowly added. The acidulated fusion is stirred cautiously with a glass rod extending under the cover. The solution is heated until all effervescence is over. The under side of the cover is rinsed off, the washings flowing into the dish. The contents of the latter are then evaporated to thick fumes of sulphuric anhydride; cool; add enough water to dissolve the sulphates, heating for about twenty minutes. Cool again. Add paper pulp. Filter and wash with 1 : 10 sul-

The apparatus shown in Photo No. 1, page 83, or Fig. 1 on page 85, omitting the pyrogallic solution, and passing air or oxygen through the apparatus instead of hydrogen, can be used for this determination.

phuric acid. Wash sixty times, allowing each washing to drain off before the next one is added. The residue on the filter is burned at lowest possible heat until pure white. The heat is then raised to blast for ten minutes. The crucible is cooled in a desiccator and weighed. The contents are blasted again, or until no further loss occurs. A few drops of sulphuric acid are added, the crucible is filled to about two-thirds its capacity with hydrofluoric acid and evaporation in a good draft to fumes of sulphuric acid follows. The sulphuric acid is driven off, the crucible is heated to bright red and weighed again. The loss of weight is the silica, which multiplied by 100 and divided by the weight taken yields the percentage of the latter oxide.*

The filtrate from the silica is passed through the reductor (page 365) and titrated for iron with potassium permanganate to first pink that lasts for a few seconds. The iron is calculated to oxide.

If alumina is also wanted, the filtrate from the silica is first precipitated in a No. 7 porcelain dish in about a 600 c.c. volume with the faintest possible excess of ammonia water which has been filtered free of any sediment or scales of glass. When the solution is faintly ammoniacal it is boiled, cooled, and ashless paper pulp added in sufficient quantity to secure rapid filtration and washing. The aluminum and iron hydroxides are washed free from sulphates with ammonium nitrate water. The washings are tested with barium chloride, and, when no milkiness forms in the former on addition of the chloride, the precipitate is given ten more washings. The filter and precipitate are burned cautiously in a weighed platinum crucible after first drying out some of the excessive amount of water held by the pulp. The paper pulp is roasted out and the ash ignited to a constant weight with a blast lamp. The precipitate is calculated as alumina plus oxide of iron. All of the phosphorus present in the graphite will be counted as alumina unless it is desired to separate it. In that event the solution should be divided before the ammonia precipitation is made. Pour it into a 500 c.c. flask. Dilute to the 500 c.c. mark with water. Mix the contents thoroughly and pour enough of the latter into a 250 c.c. flask to fill it to the mark.

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* There may remain in the crucible, after the evaporation with HF and H_2SO_4, and the ignition, a little stain of iron which should be dissolved in a little HCl, evaporated to thick fumes with a few drops of H_2SO_4, and added to the filtrate from the silica before the reduction of the iron.

This gives two portions; one is reduced with zinc and titrated with permanganate for iron. The permanganate standard is made by dissolving 0.727 gram of potassium permanganate in water and diluting it to 1000 c.c. One c.c. of this standard equals 0.001284 gram of iron. In a burned pot the iron is calculated to ferric oxide. Therefore the iron found in parts of a gram is multiplied by 10 and divided by 7 to obtain the amount of ferric oxide. It is necessary to make this calculation in all cases where alumina is asked for. In plumbago, or graphite, it is usually customary to calculate the iron to protoxide (FeO). To obtain the amount of the latter, multiply the weight of metallic iron found by $\frac{9}{7}$. These weights of oxide are then reduced to percentage in the usual way.

PHOSPHORUS AND ALUMINA

The other 250 c.c. portion of the divided sulphate filtrate is precipitated with a faint excess of ammonia, washed, roasted, and blasted to constant weight as Al_2O_3, Fe_2O_3, P_2O_5. The ferric oxide found in the 250 c.c. reduced with zinc is deducted from the total weight of the three oxides found in the second portion. This leaves Al_2O_3, P_2O_5. The phosphorus is obtained by fusing the oxides with twenty times their total weight of sodium carbonate plus their weight of potassium nitrate. The melt is dissolved in a few c.c. of water, filtered into a 5-ounce beaker, washing the filter thoroughly with ammonium nitrate water. The filtrate is acidulated with 1.20 nitric acid, boiled with a slight excess of permanganate solution (see Phosphorus in Steel), and the phosphorus is finished as in steel. The phosphorus obtained is calculated to the pentoxide (P_2O_5) as follows; For example, suppose 10 c.c. of the alkali standard were used, then $10 \times 0.0001 \times 1.63$ equals 0.00163, which multiplied by $\frac{71}{31}$ equals the phosphorus pentoxide to be deducted from the weight of Al_2O_3, P_2O_5. This leaves the alumina which came from the 0.500 gram of sample. It is reduced to percentage by the usual calculation. If phosphorus is not asked for, it is unnecessary to divide the sulphate filtrate from the silica. It can be precipitated with ammonia, filtered, washed, roasted, ignited, and weighed as Al_2O_3, Fe_2O_3, ignoring the presence of phosphorus, which is not likely to introduce a serious error. The total oxides are then fused with 10 grams of sodium carbonate, the melt dissolved in excess of 1 : 3 sulphuric acid (about 85 c.c. of the acid); reduced with zinc and titrated with permanganate. The iron is calculated to Fe_2O_3 and deducted from Al_2O_3 and Fe_2O_3 to obtain alumina.

LIME AND MAGNESIA

If lime and magnesia are asked for, the ash from the graphite is fused as before, but is acidulated with an excess of hydrochloric acid instead of sulphuric acid.

The silica is removed by evaporating twice to hard dryness and filtering between evaporations. It is washed with 1 : 10 hydrochloric acid. The filtrate and washings are precipitated with a slight excess of ammonia that has been freed from carbon dioxide as follows: The ammonia water is put in a sulphur flask fitted with a No. 6 stopper through which passes a glass tube. This tube is connected by rubber tubing with a jar such as shown in Fig. 4, page 263, filled with short pieces of stick caustic potash. The connection is with the top of the jar. The ammonia water in the flask is heated by a Bunsen burner. This drives the concentrated ammonia from the flask over into the jar of caustic potash, which removes the CO_2. The purified ammonia passes out at the bottom, and thence via more rubber tubing it reaches the glass delivery tube, which dips into a reagent bottle containing distilled water that has been boiled for half an hour and cooled without stirring. The ammonia is passed into this bottle until the water in it smells strongly of ammonia. The carbon dioxide-free ammonia is used for all separations of iron from lime.

The filtrate from the iron and alumina is concentrated to 300 c.c. and made faintly ammoniacal. If the presence of manganese is suspected, a slight excess of bromine is added, and the solution is heated until the brown flakes of manganese separate. This is not done unless the carbonate and nitrate fusion of the original ash is noticeably green.

The hot faintly alkaline filtrate is treated with 20 c.c. of saturated solution of ammonium oxalate to precipitate the calcium as oxalate. The latter is permitted to settle several hours. It is then filtered out and washed with hot water containing a little ammonium oxalate, until free of chlorine test with silver nitrate solution.* The precipitate is roasted until white and blasted to constant weight. It is weighed as calcium oxide,† which is calculated, as such, to percentage. The filtrate from the lime is acidulated with HCl, concentrated to a small volume; filtered; made slightly ammoniacal; cooled; 10 c.c. of saturated solution of microcosmic salt are added; and then the total volume is increased one-fourth with concentrated ammonia. After thorough stirring, the precipitate of ammonium magnesium phosphate is permitted to settle until the next day. It is filtered on a small filter and washed forty times with a mixture of one part of conc. ammonia and three parts of water. It is then burned at a low red heat until white, and weighed as magnesium pyro-phosphate, which contains 36.21 per cent magnesium oxide.

The filtrate and washings should be treated with more phosphate solution, and, if an appreciable precipitate forms, it is collected, washed, ignited, weighed and added to the principal residue.

SILICON CARBIDE

When complete analyses of old pots that present a green-colored fracture are made, the analytical data will give evidence of the presence of silicon existing in the reduced state, that is, not entirely as oxide. If the silica, alumina, iron oxide and lime obtained are calculated as such and to their sum is added the total carbon as found by the red lead process, the percentages may reach the impossible total of 115.8 per cent in some instances. Such pots when broken present a greenish fracture. When the writer first encountered this difficulty he was somewhat puzzled.‡ Such material cannot be burned free of black or gray residue in a stream of oxygen. This is characteristic of silicon carbide. The combination will not yield its carbon in the electric furnace with oxygen alone. It decarbonizes readily if burned with red lead. For carbon 0.300 gram of green fracture pots is burned with 4 grams of red lead. The blank due to the red lead is deducted and the carbon percentage calculated as in pots free from silicon with 10 grams of sodium carbonate, the melt dissolved in excess of 1 : 3 sulphuric acid (about 85 c.c. of the acid); reduced with zinc and titrated with permanganate. The iron is calculated to Fe_2O_3 and deducted from Al_2O_3 and Fe_2O_3 to obtain alumina.

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* Acidulate the washings with a few drops of 1.20 nitric acid before testing for chlorine.

† If the percentage of lime exceeds 0.5 per cent it is necessary to redissolve the CaO in HCl and reprecipitate it as before to insure a perfect separation of the magnesia. (See "The Complete Analysis of Limestone," etc., Chapter XVIII, Part I.)

‡ See page 191, 1st Edition Special Steels, July, 1908.

LIME AND MAGNESIA

If lime and magnesia are asked for, the ash from the graphite is fused as before, but is acidulated with an excess of hydrochloric acid instead of sulphuric acid.

The silica is removed by evaporating twice to hard dryness and filtering between evaporations. It is washed with 1 : 10 hydrochloric acid. The filtrate and washings are precipitated with a slight excess of ammonia that has been freed from carbon dioxide as follows: The ammonia water is put in a sulphur flask fitted with a No. 6 stopper through which passes a glass tube. This tube is connected by rubber tubing with a jar such as shown in Fig. 4, page 263, filled with short pieces of stick caustic potash. The connection is with the top of the jar. The ammonia water in the flask is heated by a Bunsen burner. This drives the concentrated ammonia from the flask over into the jar of caustic potash, which removes the CO_2. The purified ammonia passes out at the bottom, and thence via more rubber tubing it reaches the glass delivery tube, which dips into a reagent bottle containing distilled water that has been boiled for half an hour and cooled without stirring. The ammonia is passed into this bottle until the water in it smells strongly of ammonia. The carbon dioxide-free ammonia is used for all separations of iron from lime.

The filtrate from the iron and alumina is concentrated to 300 c.c. and made faintly ammoniacal. If the presence of manganese is suspected, a slight excess of bromine is added, and the solution is heated until the brown flakes of manganese separate. This is not done unless the carbonate and nitrate fusion of the original ash is noticeably green.

The hot faintly alkaline filtrate is treated with 20 c.c. of saturated solution of ammonium oxalate to precipitate the calcium as oxalate. The latter is permitted to settle several hours. It is then filtered out and washed with hot water containing a little ammonium oxalate, until free of chlorine test with silver nitrate

Free Silica.—This gives on a 1 gram basis 159.6 milligrams excess, which is assumed to be oxygen. This is equivalent to 30.07 centigrams of silica:

$$\mathrm{Si}+\mathrm{O}_2=\mathrm{SiO}_2.$$

$$\mathrm{O}_2 : \mathrm{SiO}_2 :: \mathrm{O}_2 : \mathrm{SiO}_2.$$

$$32 : 60.3 :: 159.6 : x.$$

$$x=30.07 \text{ centigrams } \mathrm{SiO}_2$$

to be deducted from the total silica, or $50.6-30.07=20.53$, or 20.53 per cent free silica in the pot.

Silicon Carbide.—Silica is reduced to silicon by the factor 0.4693, therefore the 30.07 centigrams of silica correspond to $30.07\times 0.4693=14.11$, or 14.11 per cent silicon. This is equivalent to 20.09 centigrams of silicon carbide.

$$\mathrm{Si}+\mathrm{C}=\mathrm{SiC}.$$

$$\mathrm{Si} : \mathrm{SiC} :: \mathrm{Si} : \mathrm{SiC}.$$

$$28.3 : 40.3 :: 14.11 : x.$$

$$x=20.09 \text{ or } 20.09, \mathrm{SiC} \text{ in the pot.}$$

Free Carbon.—The 20.09 centigrams of silicon carbide correspond to 5.98 centigrams of carbon to be deducted from the total carbon found:

$$\mathrm{C}+\mathrm{Si}=\mathrm{SiC}.$$

$$\mathrm{C} : \mathrm{SiC} :: \mathrm{C} : \mathrm{SiC}.$$

$$12 : 40.3 :: x : 20.09.$$

$x=5.98$, or $44.90-5.98=38.92$, or per cent of free carbon in the pot.

RESULTS

Excess of Oyxgen Calculated to Silicon Carbide	Excess of Oxygen Calculated to Silicon.
Per Cent	Per Cent
38 92 carbon (free)	44 90 total carbon
20 09 silicon carbide	14 11 silicon
4.37 protoxide of iron	4 37 iron oxide
15 11 alumina	15 11 alumina
0.98 lime	0 98 lime
20 53 silica	20.53 silica
100 00	100.00

SULPHUR IN POTS AND GRAPHITES

Fuse 1 gram of sample with a mixture of 10 grams of sodium carbonate ground intimately with 10 grams of potassium nitrate. Such a mixture must be heated cautiously as it will flash if heated too quickly. When the first action is over, heat until the fusion is completely molten and keep it so with the least possible heat for a half hour.* Cool; dissolve the melt with water; acidulate with hydrochloric acid in a 600 c.c. casserole. Heat with cover on until all effervescence is over, rinsing same; evaporate to dryness and finish as sulphur in ferro-silicon, page 48, of high silicon content. If such a fusion is heated too hot it will boil out of the crucible.

Standardization of Permanganate for Iron.—Weigh into a small flask 0.062 gram of oxalic acid c.p. Put into this flask 50 c.c. distilled water and 20 c.c. 1 : 3 sulphuric acid. Warm the solution until the crystals are dissolved and titrate it hot. Do not let the solution boil. It will usually require 43.1 c.c. of this permanganate to change the oxalic acid solution to a slight pink. Deduct 0.2 c.c. blank. Therefore 0.062 divided by $42.9 \times 8 \div 9 = 0.001284$, or 1 c.c. of the permanganate solution equals 0.001284 gram of iron. The value of any permanganate solution in terms of oxalic is multiplied by $\frac{8}{9}$ to obtain its iron value.

For a check, weigh 0.065 gram of oxalic acid. This will require 45.2 c.c. to render it pink. Therefore 0.065 divided by $45.0 \times 8 \div 9 = 0.001283$, or 1 c.c. standard solution equals 0.001283 gram of iron.

0.727 gram of $KMnO_4$ is dissolved in 1 liter of water for the above standard.

THE DETERMINATION OF ALKALIES IN GRAPHITE

The percentage of Na_2O and K_2O sometimes has an important bearing on the refractory properties of plumbago. To determine the percentage of alkalies, the graphite is burned away at the lowest possible heat, using oxygen. The carbon-free ash is then analyzed for the content of Na_2O and K_2O as described under the Complete Analysis of Clays. (See pages 411–412.)

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* With the present high price of platinum it would be advisable to determine the sulphur as in coke. (See page 476.)

TYPES OF PLUMBAGO (High Grade)

	Per Cent Carbon	Per Cent Ignition Water and Sulphur	Per Cent SiO_2	Per Cent Al_2O_3	Per Cent Fe_2O_3	Per Cent CaO	Per Cent MgO.	Total.
American flake...	90 99	1 41	3 74	2 37	0 95	0 40	Trace	99 86
American flake .	85 35	1 37	7.52	3 55	1 69	0 20	Trace	99 68
Alabama ...	88 25	1 33	4.44	3 35	1 25	0 62	0 48	99 72
Ceylon	91 41	1 49	4 04	0 31	1 15	0 10	Trace	98 50
Madagascar flake.	90 30	1 40	3.72	2 41	1 27	0 10	0 18	99 38
Korean graphite.	89 86	0 76	3.60	1 89	2 51	0 16	0 68	99 46
Ceylon..........	89.88	1 10	4.62	2 70	1 02	Trace	Trace	99 32
Ceylon..........	89.34	1 18	4.44	3 55	0 59	0.10	0 07	99 27

Alkalies or Mica in Graphites

When graphites are burned off in oxygen an examination of the ash often shows the latter to be a mass of more or less shining flakes of mica. The author determines the alkalies as described, and calculates the result to potash mica, Muscovite, using the formula given by Dana, $H_2KAl_3(SiO_4)_3$ or what is the same, $2H_2O, K_2O, 3Al_2O_3 \cdot 6SiO_2$, i.e., SiO_2, 45.2%; Al_2O_3, 38.5%; K_2O, 11.8% and H_2O, 4.5%. Hence by dividing the alkali percentage by 0 118, the percentage of mica is obtained assuming, of course, that it exists as potash mica, which assumption answers all purposes as either potash mica or sodium mica are bad, being very active fluxes. The following table will show what may be expected in the way of mica in natural graphites.

(1) Flake Town Flake (U. S.). . 0 36 $K_2O = 3.05$ Muscovite
(2) Crucible Flake 81631... . none none
(3) Flake Graphite 4765.... .... 0.208 $K_2O = 1\ 76$ Muscovite
(4) Ceylon Graphite........ .... 0 225 $K_2O = 1\ 90$ Muscovite
(5) Ceylon Graphite..................... 0 104 $K_2O = 0\ 88$ Muscovite
(6) Q Graphite. .. .. 0.340 $K_2O = 2.88$ Muscovite
(7) Clay County (U. S.).................... 0.322 $K_2O = 2.73$ Muscovite

CHAPTER XVI

PART II

THE COMPLETE ANALYSIS OF CLAY

Ignition Loss.—Heat 1 gram of the finely powdered sample cautiously to redness and then gradually increase the heat until the crucible has reached the full heat of a large sharp flame of a Chaddock or Méker or similar burner. Continue this heating, weighing at ten-minute intervals, until the sample no longer loses weight.

SILICA

Mix 1 gram of the finely ground clay with intimate mixture of 10 grams of sodium carbonate and ½ gram of potassium nitrate in a platinum crucible. Heat slowly at first and then apply sufficient heat to bring the clay to a quiet state of fusion. Dissolve out the fusion in water in a platinum dish. Transfer the contents of the dish to a large porcelain dish or casserole; add 100 c.c. of conc. HCl, keeping the dish covered with a watch glass as much as possible to prevent loss by spraying. Add the acid very slowly, stirring with a glass rod under the lid to mix the acid as well as practicable to prevent a sudden boiling over. Heat with the lid on until all effervescence ceases; then remove the lid, rinse off its under surface, into the dish and evaporate to dryness on a graphite bath. Cool; add 50 c.c. of conc. HCl; heat a while; then add 100 c.c. of distilled water; heat and stir until all salts are dissolved; mix in the dish a lump of paper pulp from ashless filter papers; filter through a double 11 cm. filter paper; wash out the iron, etc., with 1 : 10 HCl until no iron test can be obtained in the washings; this generally requires at least fifty washings. Evaporate the filtrate and washings to dryness; dissolve; filter and wash as before to get the last traces of silica. Smoke off gradually the two sets of filter papers in a 30 c.c. platinum crucible until white; do not rush this part of the ignition. When the residue is white, then raise the heat to the full temperature of the blast lamp; ignite to a constant weight. Then add to the crucible a half crucible full of hydrofluoric acid and a few drops of conc. H_2SO_4. Evaporate in a good draught to dryness (see page 438), and finish for silica as described on pages 47–48. The residue in the crucible after the evaporation with HF and weighing of the same is fused with 5 grams of Na_2CO_3, the melt is cooled and crucible and all is placed in the main acid filtrate from the silica which has meanwhile been evaporating in a 600 c.c. beaker on the graphite bath to 200 c.c.

When the contents of the crucible have all dissolved out, it is removed, and all of its surfaces carefully rinsed off in to the main filtrate. This main filtrate which should be now of 200 c.c. volume is made very faintly but distinctly ammoniacal and heated to just boiling for ten minutes. The precipitate, which consists mainly of hydrates of iron and aluminum, may contain notable amounts of phosphorus, titanium, and zirconium.

The ammonia precipitate is filtered hot onto a double 15 cm. ashless filter paper but before the filtration the precipitate is mixed with enough finely divided ashless paper pulp so that the mixture of precipitate and pulp will occupy three-fourths of the filter. Wash with a solution of 1 gram of ammonium nitrate dissolved in 100 c.c. of water until free of chlorine test. Redissolve the precipitate in 50 c.c. of 1 : 1 HCl. The best way to do this is to remove most of the precipitate from the paper. Pour the hot HCl through the bare paper several times; then stir the bulk of the precipitate into this same hot acid; and then pour all on the filter and wash the same free of chlorides. This filter and pulp must be saved and burned off as part of the iron and alumina, etc., as nearly always some alumina remains undissolved. Reprecipitate the filtrate and washings containing the Al, Ti, Zr, etc., hot with a slight excess of ammonia as before; filter, wash and smoke off in a platinum crucible together with the first paper and pulp; blast to a constant weight and weigh as oxide of iron, alumina, titanium, phosphorus, and zirconium. Fuse the mixed oxides with 15 grams of potassium bisulphate, heating very cautiously below redness until white fumes begin to come off and then raise the heat slowly to bright red until all is in clear solution or no further change takes place in the molten mass.

When the bisulphate fusion is cool, place crucible and all in a 400 c.c. beaker with 25 c.c. of 1 : 3 H_2SO_4 and 75 c.c. of water and heat until all is dissolved. Remove the crucible, rinsing it off into the solution. Evaporate the solution and pour it into a volumetric flask and dilute to the 200 c.c. mark. Mix well and divide into two equal parts. Pass one part through the reductor at a speed of 100 c.c. per ten minutes and titrate for metallic iron with permanganate. The iron so obtained is calculated to ferric oxide multiplied by 2 and deducted from the total oxides. The remainder is usually calculated as alumina. If it is desired to report the titanium, phosphorus and zirconium it is necessary to fuse the ignited oxides, after the final blasting and weighing, in sodium carbonate. Dissolve the melt in HCl; divide in two parts. Convert one part in sulphate by evaporating to thick fumes; redissolve in 25 c.c. 1 : 3 H_2SO_4 and 50 c.c. of water and pass through the reductor for the iron. The phosphorus in the other half is gotten out with the iron by ammonia; converted to nitrates and precipitated with molybdate solution. This can be calculated to P_2O_5 (see page 400) and deducted. This leaves the oxides of aluminum, titanium, and zirconium. These can be determined by a separate analysis, using the method given for the Analysis of Crude Zirconia (see page 202). The usual practice is to deduct the iron oxide from the total oxides and call the remainder alumina.

Lime and Magnesia

The filtrates from the two ammonia precipitations of the total oxides, page 408, which have been meanwhile evaporating in a 600 c.c. beaker are taken to 300 c.c. in slightly acid condition, having been made acid before beginning the evaporation by adding HCl. The lime is precipitated after making the solution again slightly ammoniacal, by adding to the hot liquid 40 c.c. of a saturated solution of ammonium oxalate. The lime is let stand overnight. Filter out; wash with a mixture of 10 c.c. of the oxalate and 500 c.c. and a few drops of ammonia until free of chlorides.

The filtrate and washings from the calcium oxalate are caught in a liter beaker. Add 30 c.c. of a saturated solution of sodium ammonium phosphate to the contents of the beaker and 150 c.c. of conc. ammonia and dilute with water to 900 c.c. and let stand overnight to secure the complete precipitation of the ammonium magnesium phosphate. Filter out the magnesium salt on a double 9 cm. ashless filter paper; wash it with a mixture of 50 c.c. of conc. ammonia, 5 grams of ammonium nitrate, and 500 c.c. of water until the magnesium phosphate tests free of chlorides, when the washings are acidulated with nitric acid, and a few drops of silver nitrate solution are added.

Ignite the washed phosphate at the lowest redness, after first smoking off the filter paper until it is white. This operation cannot be hurried. The weight so obtained is calculated to MgO by the factor 0.3621.

Should the lime amount to more than a per cent or two, the oxalate precipitate should be redissolved in HCl and the solution made slightly alkaline with ammonia and the lime again precipitated with oxalate to insure that it is free of magnesia. This should also be done on a new sample if the magnesia be found to be very high, in excess of 2 or 3 per cent, as lime will most likely contain magnesia although the lime be found to be low. Some of the supposed lime may be magnesium oxalate.

In case the calcium oxalate is redissolved and reprecipitated to free it from magnesia, the filtrates and washings from the two precipitations of the oxalate of lime are combined and concentrated if necessary and the magnesia is then precipitated as already described.

Complete blanks should be run on all chemicals and filter papers and deducted from all of the elements found. When a carefully conducted analysis fails to account for 100 per cent, the total of the oxides found can be deducted from 100 per cent and the remainder can be reported as "alkalies by difference" or determined by the method given.

The sulphur can be determined with sufficient accuracy on most clays by the author's method of ignition in a hot tube in a current of hydrogen carrying hydrochloric acid (see page 122). However, for an absolute method the fusion in a mixture of sodium carbonate and niter, or a mixture of sodium carbonate and sodium peroxide as given for coke on page 476 should be used as a check.

DETERMINATION OF ALKALIES IN CLAYS

Removal of Silica.—Weigh 1 gram sample into a platinum dish, 100 c.c. capacity, cover with platinum lid. Add 10 c.c. hydrofluoric acid, heat moderately for one to two minutes; then add about 2 c.c. HNO_3 (1.42 sp. gr.). Heat five minutes longer, remove lid and rinse with distilled water, then add 5 c.c. H_2SO_4 (1.84 sp. gr.), take to heavy fumes of SO_3 on stove. Let cool, add 25 c.c. HCl (1 : 1); heat for two or three minutes, dilute to 75 c.c. with distilled water, and heat until salts are in solution.

Removal of Iron and Alumina.—Transfer contents of dish to a 500 c.c. beaker; dilute to 300 c.c. with distilled water, make slightly ammoniacal with 1 : 1 ammonia; let boil two minutes, filter on double 15 cm. filter papers, catching filtrate in a 600 c.c. beaker. Wash twenty-five times with 1 per cent ammonium nitrate solution. Discard the precipitate, add a few drops of ammonia to the filtrate until it is distinctly, but not strongly ammoniacal, then add 20 c.c. of a saturated solution of ammonium oxalate and let stand several hours, preferably overnight. Filter through double 11 cm. papers catching filtrate in a 600 c.c. beaker, wash twenty times with ammonium oxalate wash (10 sat. sol. of ammonium oxalate, 5 drops 1 : 1 ammonia, and 500 c.c. distilled water); discard precipitate.

Correction for Magnesia.—Mix filtrate well, then divide exactly in half. Designate one portion (*A*), the other (*B*). Transfer one portion (*A*) to an 800 c.c. beaker, add 20 c.c. saturated solution of sodium ammonia phosphate. Dilute to 400 c.c. with distilled water, add 100 c.c. ammonia (0.90 sp. gr.) stir and let stand overnight. Filter through double 11 cm. papers, wash free of chloride with the following wash; 5 grams ammonium nitrate, 50 c.c. ammonia (0.90 sp. gr.) diluted to 500 c.c. with water. Burn off in platinum, weigh $Mg_2P_2O_7$, deduct blank and calculate to $MgSO_4$ by the factor 1.081.

Sulphates of the Alkali Plus Sulphate of Mg.—Make (*B*) just acid with H_2SO_4 (1 : 3), then add 4 c.c. in excess. Clean and weigh the original platinum dish, without lid, transfer solution (*B*) to the dish and take to dryness on stove, over moderate heat to avoid spitting. Expel ammonia salts by heating at 500° C. in a muffle furnace until white fumes are no longer given off. If salts are highly colored add 30 c.c. distilled water to the platinum dish, heat moderately until alkali sulphates are in solution, filter through 9 cm. filter papers, wash twenty times with distilled water. Clean, dry, and weigh the platinum dish, transfer filtrate to the dish and evaporate to dryness over moderate heat. When dry heat at 500° C. for five minutes, let cool in desiccator, weigh as $Na_2SO_4+K_2SO_4+MgSO_4$. Deduct $MgSO_4$ obtained from (*A*). Difference equals total alkalies as sulphates.

For general purposes, the combined sulphates of sodium and potassium may be considered as Na_2SO_4, which is multiplied by 2, and calculated to Na_2O. If both soda and potash are wanted, the following procedure is recommended:

Separation of K_2SO_4 from Na_2SO_4.—Dissolve sulphate contents of dish in the smallest possible quantity of distilled water, heat moderately for one or two minutes then transfer to a 100 c.c. beaker, add an excess of chloroplatinic acid, i.e., until precipitate settles out well or solution becomes yellow. Evaporate until solution solidifies on cooling. Add 10 c.c. of 80 per cent alcohol, stir well, let settle, then decant the supernatant liquid through a 5 cm. filter paper; avoid bringing precipitate on filter. Wash five times by decantation, using the same strength alcohol. After the final decanting, rinse contents of beaker into weighed porcelain crucible (40 c.c. capacity) with a fine jet of hot water. Wash the filter several times with a small amount of hot water, catching filtrate in the same crucible.

Evaporate to dryness at 100° C., cover, with a watch glass, then dry for one-half hour at 120° C. in an air bath. Let cool in a desiccator, remove cover, weigh as K_2PtCl_6. Deduct blanks for reagents, etc., from the gain in weight of crucible and calculate to the remainder K_2SO_4. Deduct the weight of the K_2SO_4 from the combined sulphates of sodium and potassium; thus giving sodium sulphate by difference. Calculate percentage of K_2O and Na_2O on a basis of one-half the original weight taken for analysis.

$$\begin{aligned} K_2PtCl_6 \times .35846 &= K_2SO_4, \\ Mg_2P_2O_7 \times 1.0811 &= MgSO_4, \\ MgSO_4 \times .3349 &= MgO, \\ K_2SO_4 \times .5406 &= K_2O, \\ Na_2SO_4 \times .4364 &= Na_2O. \end{aligned}$$

For a standard, c.p. sodium chloride and potassium nitrate should be put through all operations simultaneously with the tests. Any excess is deducted as a blank for each element determined.

CLAYS HIGH IN ALKALIES AND NOT GOOD FOR REFRACTORIES

	No 1	No 2	No 3
Ignition	8 72	5 72	6 18
Silica	62 92	71 43	65 20
Alumina	22 95	17 78	20 38
Iron oxide	3 01	2 15	2 84
Lime	0 36	0 24	0 38
Magnesia	0 36	0 41	0 61
Alkali (Na_2O)	1 99	1 97	4 04
	100 31	99 70	99 63
Sulphur	0 210	0 088	0 057

ANALYSES OF CLAYS OF GOOD REFRACTORY PROPERTIES

	Silica.	Iron Oxide	Alumina	Lime	Magnesia	Ignition	Sulphur	Total.
H. W	54 98	3 31	28 03	0 66	0 55	11 38	0 11	99 02
Oak	52 60	4 12	27 54	0 82	0 91	13 74	0 190	99 92
Southern	53.80	3 07	27 97	0 44	0 54	12 58	0 044	98 44
M-N	47 80	2 87	35 95	0 30	Trace	13 26	0 025	100 20
U. S. A	53 12	2 63	29 41	0 64	0.54	12 90	0 021	99 26

CHAPTER XVII

PART I

THE ANNEALING OF STEEL

Annealing Temperatures.—FIRST. Cast steel of all kinds that has *never been reheated* should be first brought to a temperature of 850°–900° C., and held there for one hour. The heat should then be lowered as quickly as possible to 700° to 720° C. and held at that temperature for ten to twelve hours. The pipes can then be drawn and the steel can be cooled as quickly as desired. The fact is, that if the steel is once perfectly annealed, it can be withdrawn from the furnace, thrown into water and it will be as soft as ever. The author took two pieces of steel from the same saw plate and annealed them, one lying on top of the other, until he knew both were perfectly annealed. He then withdrew the pieces from the furnace. One was thrown directly from the annealing furnace into a bucket of cold water while still at the *annealing* heat. The companion piece was cooled in the air. Both pieces were then pulled in the testing machine and registered identically as to tensile strength and elongation, etc. Steel once perfectly annealed can only have its softness impaired by heating above the annealing range. Rapid cooling of *perfectly* annealed steel has no effect whatever on its softness.

However, if the annealer has lowered the heat before the steel has been entirely annealed, or in other words has not held it long enough within the range of temperature where that particular steel anneals most quickly, he stands a better chance of getting his steel eventually soft enough for the purpose intended by burying it in ashes or lime. He thus, in reality, holds it longer within the range of temperature where steel anneals *slowly*. That is, the steel passes more slowly through the range of *slow* annealing, being the temperatures below 720° C., than if it had *not* been surrounded by more or less non-heat conducting substances.

SECOND. The author has found that plain carbon steels, no matter whether the carbon be 0.50 per cent or 1.40 per cent, anneal best and most quickly between 700° and 720° C.

This is also true of most chrome-tungsten and chrome-molybdenum steels. It is particularly noticeable in high-speed steels, for if one wishes to drill a high-speed test he can render it soft enough by annealing it for one-half hour at 720°, whereas it will require two to three times that length of time to accomplish the same softening at lower ranges.

THIRD. On the other hand, high manganese and high nickel content lower the annealing heat. Seven per cent nickel steel anneals to the perfectly annealed state of the carbon at 520° to 550° C.* Again, the author has succeeded in softening Hadfeld's manganese steel previous to 1908 so that it could be drilled without dulling a high-speed tool at a temperature of 520° to 550°. The specimen of this steel that the author first experimented with was of the following analysis:

	Per Cent
Carbon	1.40
Manganese	13 42
Silicon	0 043
Phosphorus	0 047
Sulphur	0 030

Plates of this steel, before annealing, could not be drilled even with a high-speed drill. After twenty-four hours' annealing a plate was drilled without sharpening the bit and the latter drilled the plate without "screeching." In fact, four holes were made in such a plate without resharpening. These plates were then taken to the planer and machined easily, but they presented the peculiar property of being very brittle. The condition of the carbon by the acid annealing test showed that the carbon had attained almost entirely to the perfectly annealed state.

FOURTH. Steel that has been reheated and rolled or hammered need not necessarily be heated above 720° C.† However, if the furnace is heated to 850°, for example, and a lot of steel is charged into it, it can be brought to 720° more quickly. The large body of cold steel will absorb its surplus heat.

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* Read remarks given on page 422 on the annealing temperatures of different alloy steels.

† The author has been able to get better anneals on many forged chrome-tungsten steels by first heating the same through for an hour or so at 850° to 900° C. and then holding at 720° C.

Overheated Steel.—If steel ingots are allowed to lie in soaking pits or reheating furnaces at temperatures approximating welding heats for considerable time, the annealer's task will be greatly complicated, as such steel is much harder to bring into the annealed state.* Bad cases of overheating or prolonged soaking at high heats will require two or three times as long to anneal at the regular temperature. There seems to be nothing to do in such cases but to re-anneal until the carbon is finally brought again into the perfectly annealed condition.

FIFTH. Some steels in the original unforged casting that are of the usual high-speed analysis except that the chromium is in excess of 5 per cent and the carbon is 0.90 to 1.20, require unusually long periods of annealing to render them drillable. The annealing temperature for such steels is below 700° C.

SIXTH. Steel that has been heated to 800° to 850° C. and quenched quickly in water or oil will attain the perfectly annealed condition within thirty minutes to one hour's time at a temperature between 620° and 690° C., whether the carbon be 0.50 or 0.90 per cent, that is, a quenched steel anneals at a lower temperature than when unquenched, and in less time.

Formation of Graphitic Carbon and Black Fracture.—On three different occasions the author was called upon to investigate the temperature most favorable to the formation of graphitic carbon, or in other words, to ascertain the real cause of its presence. As a result of extended experimental annealing of cold rolled steel he has come to assign the cause largely to annealing only, within a range of temperature that causes the carbon to assume the uncombined state.

As mentioned, on three different occasions, three different lots of cold rolled steel, coming from different steel works, were subjected to prolonged annealings, and the progress of the formation of the graphitic carbon was noted.

In two lots, the cold rolled steel was free from even traces of the graphite at the beginning of the anneals. Anneals were continued in some instances for 100 hours, but most periods did not aggregate over forty hours. Anneals were interrupted at eight-

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By reason of the very coarsely crystalline structure formed by the excessive heat.

to twelve-hour intervals to make annealing and graphite tests. Further, a 1.30 carbon tool steel *ingot* was put in a lathe and turned down until there was nothing left of it but a ⅝-inch rod. By prolonged annealing between the range of 660° to 700° black fracture was produced. This was raw cast steel that had never been hammered or rolled or forged in any way. The conclusions are as follows:

FIRST. The higher percentages of carbon yield the black fracture most quickly, the range from 1.20 per cent carbon and above being the most favorable. Percentages under 1.00 per cent carbon are perhaps free from appreciable amounts of graphitic carbon, at least under any conditions likely to be met with in practice.

SECOND. The temperature most favorable to the quick formation of graphite lies between 660° and 700° C.

THIRD. The least favorable temperature for its formation, within the annealing and *cold rolling* range, is below 600°. The other extreme of temperature, 720° C., is also less favorable to its formation, but scaling goes on so fast as to give undesirable finish.

Also the naturally dark, dense color of the cold-rolled steel grain intensifies the blackness of the graphitic fracture, giving to it an even texture, making it far more apparent in the earlier stages of graphite formation. Graphite formation in an unworked casting is not nearly so noticeable, although it may have progressed far. The precipitation seems to take place more in spots. The working of steel during or before graphite growth gives it an intense black clothlike appearance in the fracture.

FOURTH. The reason that black fracture is associated with cold rolling is that during this process the steel is worked and repeatedly reheated within the range of temperature where graphite forms rapidly. The steel has really had a series of anneals between 660° and 700° C.

FIFTH. The longer the anneal is continued *at any annealing* temperature, the more graphite will be formed.

Prior to cold rolling, that is, when the steel gets its very first anneal for softening purposes only, hold it at 700° to 720° C. Keep it as near the highest annealing heat as possible, as by so doing a quick anneal is obtained without formation of graphite.

But when reheatings occur during cold rolling do this reheating at the lowest heat practicable, for around 580° to 600° C. graphite does not form as fast as at 660° to 700°, nor does scale. *Let the periods of annealing and reheating be as short as possible.*

Sixth. By heating steel to 950° to 1000° C. for one or two hours, then turning down the gas so that the steel cools in the furnace to 660° to 700°, and continuing to anneal at the latter temperature for a given length of time, graphite can be eventually formed in steel with carbon as low as 1.04 per cent. Therefore steel that is to be cold rolled should not be allowed to remain long in soaking pits or heating furnaces at high temperatures.

Steel containing chromium is not likely to contain graphite even with carbon as high as 1.27 per cent and chromium as low as 0.6 per cent. The author succeeded in starting a graphitic formation in such a steel only by heating it to 900° to 1000° C., for an hour or two before annealing at 660° to 700° C. In neither this instance nor in the case of the 1.04 carbon plain steel did there seem to be any appreciable tendency for a gradual growth of the graphite due to prolonged annealing only, even after the eleventh trial, making considerably over 100 hours' anneal. Perhaps if these samples had been again heated to 1000° before each of the eleven anneals, an appreciable growth of graphite would have been noted. In neither instance was there enough graphite formed to be noticeable in the fracture.

To detect small amounts of graphite dissolve 0.100 gram of sample in a 152.4 mm. by 16 mm. tube (6 inches by 16 mm.) with 4 c.c. 1.20 nitric acid and heat on a water bath in boiling water for two hours in the case of chrome steel and one hour in plain carbon steel. Of course, where the chromium content exceeds a few tenths of a per cent carbides of chromium are formed that are in no sense graphitic. For this reason the acid test for graphite is not available in such steels. Permit the solution to stand for several hours without agitation of the same to detect traces of graphite which can be plainly seen in this way in the bottom of the tube.

Acid Test for Annealing.—* Dissolve 0.100 gram of sample in 4 c.c. of cold 1.20 nitric acid. Examine immediately in daylight. If the undissolved carbon is flaky and floats about in the solution the steel is not annealed at all. It is in the condition in which it left the rolls or hammers. If on the other hand the carbon is in an extremely fine state of division, so much so that it does not separate in flakes at all, but rather tends to run up the sides of the test tube in a thin film, then the annealing is perfect and the steel has reached the highest degree of softness.

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* Reject surface drillings to the depth of at least one-eighth of an inch when taking a sample for annealing test.

In perfectly annealed steel this finely divided annealed carbon will remain in almost complete suspension for some minutes. Indeed it cannot be seen to collect and settle as flakes, but settles imperceptibly, after some time, so that there exists a collection of fine powder, rather than flakes, in the bottom of the test tube. An ordinary 6-inch by 15-mm. carbon test tube * is best suited for these tests. Then, if it is desired to examine the sample for graphitic carbon, the tube is put at once on a water bath in boiling water for one hour. By that time all of the combined carbon will have gone into solution and the graphite will be collected in a coal-black residue in the bottom of the tube.

The operator soon learns to pronounce to an absolute certainty whether the steel is *perfectly* annealed or not. He also can judge whether much or little graphitic carbon is present.

This annealing test is carried out in ten minutes, and enables the chemist to pronounce unfailingly on the quality of the annealing before the steel is shipped to the customer. It gives a perfect control over the work that is being done by the man in charge of the annealing. A scale of annealing can be established. It has been the author's custom to call perfect annealing, 5°. Good enough for all practical purposes, 4½°. Moderately good, 4°. Partially annealed, 3°, and so on. The quicker the carbon forms in flakes and separates, the poorer the annealing. As stated, perfectly annealed carbon does not separate in flakes at all.

Annealing Test When Alloys are Present.—When from 0.1 per cent to 1 per cent chromium is present in steel the annealing *carbide* is formed and acts differently from carbon in plain steel. It forms almost coal black; is not flaky; but the individual grains are coarser than in plain carbon steel.

A well-annealed chrome carbide within the above chromium content forms in minute coal black grains that settle rapidly to the bottom of the test tube. The quicker the grains form, the blacker they are, and the more rapidly they settle to the bottom, the better the anneal.

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* Test tubes must be scrupulously clean, free from the slightest film of grease, or dirt, or other coating.

This peculiarity constitutes an infallible test for the presence of chromium in steel, but the latter must be perfectly annealed to show as small a quantity as 0.1 per cent chromium in 0.100 gram of sample. More experience is required to pronounce on the annealing of chrome steel by the acid test.

In well-annealed steel containing 3 per cent of chromium and over, the carbide is coal black but does not settle to the bottom nearly so fast as does the carbide found in perfectly annealed steel of 1 per cent chromium and under. The grains settle slowly, and there is a well-defined film running up the walls of the test tube, but the grains should be in the finest state of division.

Plain tungsten steel, in the perfectly annealed state, gives practically the same appearance as ordinary carbon steel when tested for annealing.

Nickel and manganese steels act exactly as plain carbon steel when perfectly annealed. The color of the finely divided annealed carbon has perhaps more of a brown shade in high manganese and nickel steels, but it does not settle any faster than in plain carbon steels. One of the greatest difficulties in annealing steel is to obtain uniform heat throughout the entire furnace. The dividing line between a good annealing heat and hardening temperature is very sharp. The author has had a piece of steel but 2 inches long exhibit perfect annealing on one end, while the other end had passed into the hardening range. He has also another piece that shows black fracture on one end, and the other end less than 2 inches away shows no trace of black fracture. These phenomena are due to unequal temperature in the furnace.

An annealing furnace should have several pyrometer couples located in different parts of it.

Calibration of Pyrometer Couples.—Pyrometers should be checked at regular intervals. The most convenient method is to use the freezing-point of c.p. sodium chloride. This substance freezes at 804° C. A few ounces of the salt can he heated somewhat above its melting-point in a muffle furnace. The salts should be melted in a good clay crucible of low iron content such as the best grade of Denver crucible. The crucible is removed quickly from the furnace and placed in a receptacle made of infusorial brick of just the right size to hold the crucible. The apparatus can be covered with a non-heat conductor provided with a hole to admit the fused end of the couple. The bare wires of the platinum-rhodium couple can be put directly in the fused salt. The temperature of the molten salt is then read every ten seconds; and when the drop in temperature remains stationary for 100 seconds, this reading is taken as the freezing-point. If the galvanometer of the instrument reads lower than 804° C., this number of degrees must be added to its future readings. If it reads so many degrees higher than 804° C. its readings are reduced by that amount.

If desired, the instrument can be also calibrated against the freezing-point of potassium sulphate (K_2SO_4). which freezes at 1072° C. And for a low range, against that of potassium nitrate, which freezes at 337° C. Taking all three salts, three freezing-points are obtained from which a curve can be plotted.

The freezing-point of salt (NaCl) is the most accurate one of the three. Fresh salts should be used each time. Barium chloride c.p. (anhydrous) freezes at 955° C. This salt can also be applied to the purpose.

It should be stated that the ten second interval in the readings of the dropping temperature was chosen because it was found that, with the heat insulation chamber used, the temperature dropped at regular intervals of ten seconds. This interval of drop can be lengthened by increasing the thickness of the chamber walls and shortened by using a thinner layer of infusorial earth in the walls.

In like manner a change in the heat insulation layer will change the time period of the much longer pause noted above and that occurs when the salt freezes.

CHAPTER XVII

PART II

(1) FURTHER ANNEALING TEMPERATURES. (2) SURFACE DECARBONIZATION

SUPPLEMENTING the annealing temperatures given on page 415, one can calculate *approximately* the best annealing temperature for manganese and nickel steels by deducting from 720° C., 18½° for every per cent of manganese or nickel present; and on account of the similarity of cobalt to nickel the presumption is that the rule holds good for cobalt also. To determine *exactly* the best annealing temperature, one should first determine the critical point of the steel and then anneal it just under the critical point (Ar_2). If one has no apparatus for critical point, then recourse can be had to the above calculation. The result can be checked by the acid annealing test given on pages 418 and 419 and the annealing trials continued until the chemical test shows the annealing is perfect.

Annealing Temperature for Chrome-Manganese Steel and Chrome-Nickel Steel.—In such steels there exists two independent annealing temperatures, that is, the steel must be given an annealing as though it were chrome steel or first soaked at 850° C. and then held at about 720° C. and then the temperature should be lowered and the nickel annealed as though it were a manganese steel, or a nickel, or cobalt steel, only.

Some of these manganese-chrome steels require as low as 350° to 450° C. to soften the manganese combination therein.

Twelve per cent nickel steel of low carbon (0.50 per cent carbon) anneals well at about 500° C. Highly alloyed chrome-tungsten-vanadium steels with carbon over 1 per cent, alloyed further with 2 or 3 per cent of copper, must first be annealed for some hours at about 850° C. and then, curiously enough, must be given as low an annealing as though 10 to 13 per cent of manganese were present. It is necessary to perform the annealing in this way before the steel can be drilled at all, even with the best Rex AA drill. The same kind of a steel with low carbon of about 0.60 per cent C. does not require the low anealing temperature. This is a striking example of the fact that carbon has a marked influence on the annealing temperature in some cases.

The Formation of "Bark" or Decarbonized Surface on Pipe-Annealed Steel.—Several years ago the author investigated the cause of this troublesome soft surface and his conclusions were published in the following paper:

THE FORMATION OF WHITE SCALE ON STEEL AND THE SURFACE DECARBONIZATION OF PIPE-ANNEALED STEEL * †

When bars of steel are annealed in pipes, with charcoal, to produce a scale-free, frosted, metallic finish, there is frequently found at the surface of the metal a coarsely crystalline structure *H*, *G*, Fig. 34, that is much lower in carbon content than the remainder of the bar. Such steel will not harden file-proof on the outside. It is rejected for that reason by makers of twist drills, though this defect be so slight as to require a magnifying glass for its detection.

In pipe-annealing the bars are put in a steel tube that is welded shut at one end. The spaces between the pieces are filled in with wood charcoal. The open end of the pipe is plugged with fire brick, fire clay, and a disc of plate steel. A small vent hole is located at one end of the pipe to permit the escape of the large quantity of carbon monoxide that is generated by the reaction between charcoal and the air yet remaining in the vessel. As apparently dry charcoal often holds considerable moisture in its pores, some water vapor must also be liberated.

The superficial decarbonization *G*, *H*, *I*, Fig. 34, is at times much more pronounced than at others. The author became interested to investigate the process with a view to discovering

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* From a paper read at the March, 1909, meeting of the Pittsburgh Section of the American Chemical Society.

† Reprinted from the Journal of Industrial and Engineering Chemistry, Vol. I, No. 7, July, 1909.

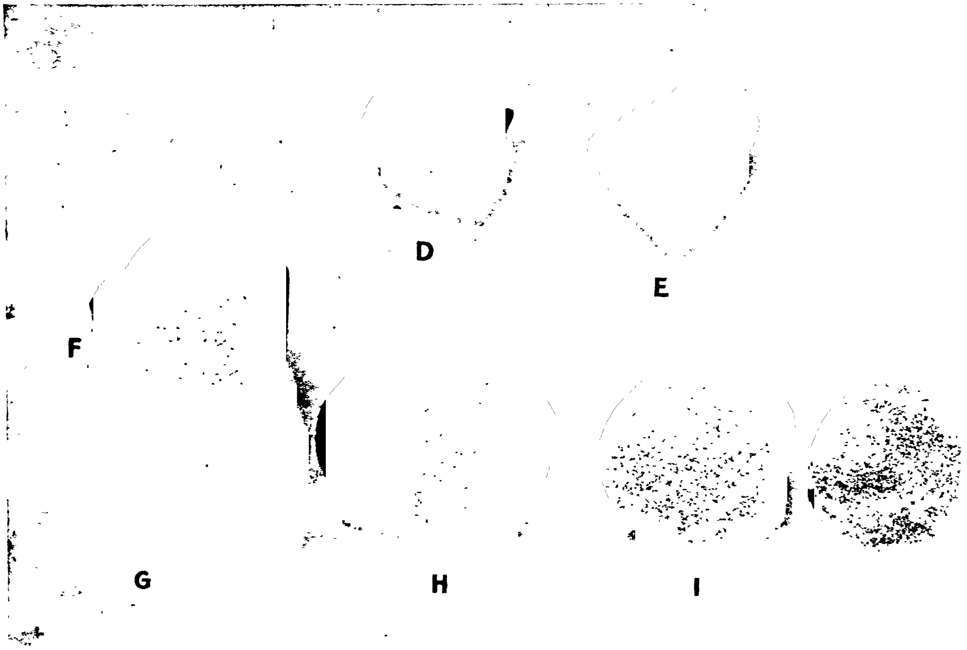


Fig. 34.

the primary cause of this very objectionable feature of annealing in a closed tube.

In the first place it was soon noted that the condition frequently exists in steel before it reaches the annealer, due to forging at too high temperatures.

Again, it was deemed possible that the scale, always existing on the steel when it is put in the pipes, might react with the charcoal to form CO_2. Further, that the latter gas would, under the existing conditions, decarbonize the steel by the reaction $CO_2+C=2CO$.

To test this theory some five-eighth inch Rd., high-carbon steel rods were placed in a porcelain tube and heated for eighteen hours with a slow stream of pure, dry carbon dioxide passing through the enclosure. The following points were noted:

FIRST. A glittering black scale was produced on the fractured or otherwise unpolished surfaces of the bars. On fracturing the latter, a distinct ring of coarse crystals was found to exist at the margin of the fractures. This scale has a curious property of adhering in a thick, sparkling black mass on rough fractured surfaces, but when polished steel is exposed, at a red heat, to the attack of CO_2, only a black discoloration resulted. The scale referred to, proved on analysis, to be Fe_3O_4. This experiment showed that carbon dioxide may cause "bark" (surface decarbonization) but not to a marked enough extent to offer a satisfactory explanation.

SECOND. Some pieces of the same bar were heated in a stream of pure, dry hydrogen. A frosted metallic surface was produced and also a slight "bark." Hydrogen, therefore, will decarbonize steel by forming hydrocarbons.

THIRD. Next, a piece of the bar was heated in the closed porcelain tube, packed loosely with charcoal. First air was expelled, but, as the heat attained slight redness, large quantities of CO escaped at the outlet end. After an eighteen-hour heating, at about 750° to 780° C., a handsome frosted, metallic surface had displaced the black oxide and much decarbonization was noted. The carbon content of the bar before annealing was 1.08 per cent. The decarbonized zone yielded but 0.84 per cent.

FOURTH. Thinking that CO gas might be the active agent in (3), a small clay boat was filled with about a tablespoonful of charcoal. The boat was then placed in the tube with a piece of the steel and the usual period of heating followed. The result was the same as in the third experiment.

NOTE. Annealing in a stream of natural gas produced a sooty exterior and a heavy "bark" (see *J*, Fig. 34.)

FIFTH. The fourth trial suggested annealing a piece of steel in an EMPTY, CLOSED TUBE with no CHARCOAL or other reducing substance. No attempt was made to remove the air except as it was partially driven out at the vent end by expansion. The only precaution taken was to prevent indrawing of more air, at *any time*, while the tube was *hot*. The same result was obtained as is shown in the white bars at *C*, Fig. 35, that is, an aluminum-like surface with great decarbonization underneath. This experiment was repeated with steel containing but 0.10 per cent carbon and also with steel containing large quantities of chromium and tungsten. The 0.10 carbon steel is given at *B*, Fig. 35.

The author felt that he had now reached the first goal and that the most active agent in surface decarbonization is the rust or scale which is actually reduced to metal at the expense of the carbon in the steel to which it adheres:

$$4C + Fe_3O_4 = 3Fe + 4CO.$$

In this connection the question arose, would steel with an extra heavy, loosely adhering scale perform in like manner. Or, in other words, is close contact necessary for reduction. To settle this query a small piece of quarter octagon of saw analysis was given a prolonged heating in an *open* muffle at about 850° C. This treatment blistered the bar with a thick scale that was so loose that the sample had to be transferred to the annealing tube quite carefully to prevent the scale from being jarred off. After fifteen hours' heating no change was noted, that is, the scale was still black. After a second heating of eighteen hours the *surface* of the scale presented a slight *grayish* caste. After a third period of eighteen hours' heating it was found that the heavy black scale was gone and, in its place, a *white*, loosely adhering, aluminum-like scale existed on the steel. Here, apparently, the black scale had begun to reduce on its top surface first.

This fact pointed to the existence of a reducing gas in the tube.

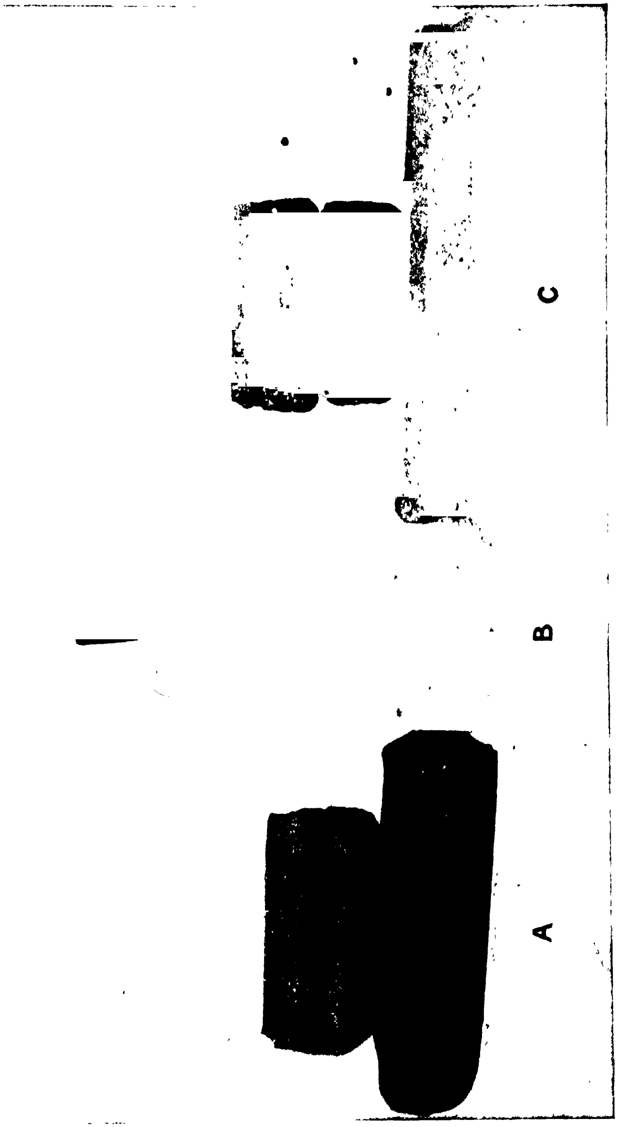


FIG. 35.

SIXTH. The author then placed a piece of high-carbon steel in the tube, together with a porcelain boat containing some hard, semi-fused iron oxide obtained from a carbon combustion of steel drillings in oxygen. This hard, baked mass *D*, Fig. 34, was given eighteen hours' heating at a temperature of about 850° to 900° C. The porcelain boat was removed and found to contain, instead of a dense baked mass, a loose, friable substance, and that the volume of it exceeded the original about 2½ times. The steel that had been in the tube was then fractured. It was exceedingly tough and disclosed a heavy surface decarbonization *G*, Fig. 34. The loose sponge of oxide was put back in the tube with a fresh piece of steel and given a second heating. This time the substance *E*, Fig. 34, in the boat had become light-gray in color and was no longer friable but was now adherent and almost sticky in its clinging fibers. This material assayed 98 per cent metallic iron and, on being cut with a knife blade, presented a metallic luster. It occurs that here is a means of preparing pure metallic iron from pure oxide by heating it in a closed tube with a sealed vent (the author used concentrated sulphuric acid for a seal), together with a piece of low sulphur, high-carbon tool steel. Before turning off or lowering the heat it is, of course, necessary to close all vents perfectly, otherwise air will be drawn in the tube and metallic iron surfaces will lose the aluminum-like luster and become blued. Metallic iron so prepared should certainly be free of occluded hydrogen, which constitutes an objection to electrolytic iron. Some specular iron ore was ground to a red powder and then reduced to a gray powder in this way.

A piece of steel *A*, Fig. 35, that had been lying in water for weeks and was covered with both black and yellow oxides was heated in an empty, sealed tube. The result was a white metallic surfaced sample. A piece of blue steel was heated four hours in an empty tube and the blue surface was replaced by a white aluminum-like one.

SEVENTH. Further experiments developed the fact that this white scale forms much more rapidly at high temperatures, that is, those above 700°. The higher the heat the more rapid the transformation from rust and black scale to the white and metallic scale. This white scale takes on the white appearance long before it is entirely reduced to metal. The author has had white scale that would be brittle and grind to a black powder. However, when the reduction is complete the scale is no longer brittle and cannot be powdered, but is entirely metallic in its properties.

EIGHTH. The corollary from the fact that white scale forms more slowly below 750° C. is that, at still lower ranges, perhaps below 650°, it may not form at all. Further experiments covering this point will be made.

NINTH. By annealing steel in a closed tube with a small vent to permit egress of gases but sealed against ingress of air, at temperatures close to 700° C., the surface decarbonization is so slight that no ring of coarser crystallization can be detected. Only a cupped effect can be noted around the margin of the fracture (see *F*, Fig. 34), yet such steel will take on a suggestion of the aluminum-like finish. Here the surface decarbonization is confined to the thinnest skin. Such steel hardens file-proof immediately under this extremely thin zone.

TENTH. By annealing steel that had been polished free of all rust and scale, in a tube from which ALL OXYGEN had been expelled by CO, no surface decarbonization was noted and the steel hardened file-proof. The CO was generated by heating wood charcoal.

ELEVENTH. A rod of polished steel was dipped in a solution of copper sulphate until it was plated with metallic copper. After heating this rod in a closed tube, *without* expulsion of the air, for a few hours, the rod was removed from the tube and was found to be coated with a handsome appearing metallic copper. During this experiment the tube was sealed against ingress of oxygen.

TWELFTH. By heating tungsten trioxide in a closed porcelain tube, and together with, but not in contact with, either a piece of steel or steel drillings, the author was able to produce metallic tungsten powder of 99.98 per cent purity. The temperature required for this experiment was 1100° C. The tungsten oxide was in one porcelain boat and the steel drillings were in another.

CHAPTER XVIII

Part I

THE COMPLETE ANALYSIS OF LIMESTONE AND MAGNESITE

(1) Dissolve 0.9 or 1.0 gram of the sample in 50 c.c. of 1 : 1 HCl in a No. 5 ($4\frac{3}{4}$ inch) covered dish. Boil until all action is over, remove the cover and evaporate to dryness on the graphite bath; heat until the smell of acid is practically all gone. Cool; add 40 c.c. of 1 : 1 HCl; cover; boil with the lid on and evaporate to 20 c.c.; add 50 c.c. of water; boil with the cover on for a few minutes; add ashless paper pulp; filter; wash, first with dilute 1 : 40 HCl, and then with water until 20 drops of the washings do not give even a slight milkiness with silver nitrate solution. Smoke off the paper in a platinum crucible and then raise the heat to bright redness until all black is gone and the ash in the crucible is from a pure white to a gray depending on the grade of the limestone. Weigh the ash after it has been cooled in the desiccator and calculate it as insoluble residue. Fuse this insoluble residue, which consists of silica contaminated with some lime, oxide of iron and magnesia, with twenty times its weight of anhydrous sodium carbonate; dissolve the residue out in water in a platinum dish with heat or in porcelain in the cold in HCl if no platinum dish is available; acidulate the water solution with an excess of HCl; heat with the lid on until all spraying due to the escape of carbon dioxide is over and evaporate to hard dryness, twice, filtering after each evaporation. Moisten the residue in the dish with 10 c.c. of conc. HCl; heat; add 50 c.c. of water; boil five minutes; add a little paper pulp; filter and wash as in the case of the insoluble residue; ignite until the ash is pure white and weigh as pure silica. As an extra precaution against the presence of sodium salt it is more accurate to volatilize silica as in steels with HF and a few drops of H_2SO_4.

(2) The filtrate from the pure silica is added to the main filtrate and washings obtained from the insoluble residue. These combined filtrates contain all of the calcium, magnesium, iron, and aluminum. A slight excess of ammonia is added to the nearly boiling filtrates to precipitate the iron and aluminum. A little paper pulp is well stirred in; the hydroxides are filtered off; washed with water; redissolved, and precipitated as before to insure the complete separation of the calcium and magnesium from the iron, etc. The reprecipitated iron, etc., is washed free of chlorides with water and ignited to a constant weight in a platinum crucible as Fe_2O_3, Al_2O_3 and calculated as such to percentage.

The filtrates from the double precipitation of the iron are combined, evaporated to 600 c.c., heated to boiling, and the calcium is precipitated with 50 c.c. of a saturated solution of ammonium oxalate. This amount of oxalate is added not only to precipitate the calcium but to insure an excess of the oxalate in sufficient quantity to hold the magnesium in solution as the latter is soluble in an excess of the oxalate. When magnesium is present in considerable quantity, it has a decided tendency to precipitate some time after the oxalate is added, forming crusts of magnesium oxalate. To reduce this formation to a minimum, the excess of free ammonia should be small. Do not boil the solution after the ammonium oxalate has been added. Always redissolve and reprecipitate the oxalate of calcium as described in the method and in the way just given, avoiding much excess of free ammonia.

The oxalate of calcium should stand for at least several hours when it is filtered off, after mixing it with considerable paper pulp. Wash it with oxalate water (5 grams of ammonium oxalate dissolved in 500 c.c. of water) until the washings, acidulated with a few drops of nitric acid, fail to give a reaction with silver nitrate. The calcium oxalate, to insure against the co-precipitation of a portion of the magnesium, should be dissolved in HCl, the filter thoroughly washed and the calcium reprecipitated as before, this time adding 25 c.c. of the ammonium oxalate. The reprecipitated calcium oxalate is filtered, washed, ignited, and finally blasted to constant weight as calcium oxide, which weight multiplied by 1.7847 gives the equivalent weight of calcium carbonate which is calculated to percentage as such.

The filtrates and washings from the two precipitations of the calcium oxalate are combined and evaporated to about 200 c.c. in the case of limestone, or to about 400 c.c. if magnesite. The solution, which should contain no crystals, is made slightly ammoniacal and 20 c.c. of a saturated solution of microcosmic salt are added if the sample is limestone; if it is magnesite, 50 c.c. of the latter salt are used. The volume is then increased one-third with strong ammonia. The solution and precipitate are given a prolonged stirring, especially if the precipitate is slow in forming. After twelve hours have elapsed the ammonium magnesium phosphate is filtered off and washed free of chlorides with a mixture of 80 c.c. of conc. ammonia, 400 c.c. of distilled water and 5 grams of ammonium nitrate. The washed precipitate is smoked off in a platinum crucible and then the heat is raised to bright redness. The residue in the crucible is stirred from time to time until it is finally pure white. It is cooled in a desiccator and weighed as magnesium-pyrophosphate, which multiplied by 0.7572 gives the equivalent weight of magnesium carbonate.

The calcium oxide and the magnesium pyrophosphate, after having been ignited to a constant weight, should be dissolved in HCl and the milligram or two of silica that is almost invariably present should be filtered off, washed, weighed, and deducted from the calcium oxide and the magnesium phosphate before the final calculations to carbonate are made.

The filtrates and washings both from the calcium oxalate and the ammonium magnesium phosphate should be tested in every instance with further additions of the precipitants to make sure that precipitations have been complete.

SOME ANALYSES OF LIMESTONE

	No 1	No 2	No 3	No 4	No 5.	No 6
	%	%	%	%	%	%
Calcium carbonate	94.20	93.21	94.71	98.80	81.35	90.30
Magnesium carbonate	1.51	1.44	2.02	0.26	3.08	1.86
Oxides of iron and aluminum	0.09	3.20	1.46	0.26	3.12	2.46
Silica or insoluble residue	4.16	1.80	1.46	0.31	11.68	5.26

Samples Nos. 2, 3, and 4 are good limestones for basic open hearth purposes, being low in silica and over 93 per cent in calcium carbonate. Nos. 1 and 6 are doubtful and No. 5 is distinctly bad.

(2) The filtrate from the pure silica is added to the main filtrate and washings obtained from the insoluble residue. These combined filtrates contain all of the calcium, magnesium, iron, and aluminum. A slight excess of ammonia is added to the nearly boiling filtrates to precipitate the iron and aluminum. A little paper pulp is well stirred in; the hydroxides are filtered off; washed with water; redissolved, and precipitated as before to insure the complete separation of the calcium and magnesium from the iron, etc. The reprecipitated iron, etc., is washed free of chlorides with water and ignited to a constant weight in a platinum crucible as Fe_2O_3, Al_2O_3 and calculated as such to percentage.

The filtrates from the double precipitation of the iron are combined, evaporated to 600 c.c., heated to boiling, and the calcium is precipitated with 50 c.c. of a saturated solution of ammonium oxalate. This amount of oxalate is added not only to precipitate the calcium but to insure an excess of the oxalate in sufficient quantity to hold the magnesium in solution as the latter is soluble in an excess of the oxalate. When magnesium is present in considerable quantity, it has a decided tendency to precipitate some time after the oxalate is added, forming crusts of magnesium oxalate. To reduce this formation to a minimum, the excess of free ammonia should be small. Do not boil the solution after the ammonium oxalate has been added. Always redissolve and reprecipitate the oxalate of calcium as described in the method and in the way just given, avoiding much excess of free ammonia.

The oxalate of calcium should stand for at least several hours when it is filtered off, after mixing it with considerable paper pulp. Wash it with oxalate water (5 grams of ammonium oxalate dissolved in 500 c.c. of water) until the washings, acidulated with a few drops of nitric acid, fail to give a reaction with silver nitrate. The calcium oxalate, to insure against the co-precipitation of a portion of the magnesium, should be dissolved in HCl, the filter thoroughly washed and the calcium reprecipitated as before, this time adding 25 c.c. of the ammonium oxalate. The reprecipitated calcium oxalate is filtered, washed, ignited, and finally blasted to constant weight as calcium oxide, which weight multiplied by 1.7847 gives the equivalent weight of calcium carbonate which is calculated to percentage as such.

By the equation $2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$; $2KMnO_4 = 5H_2C_2O_4$, hence $2KMnO_4 = 5Ca$, or 316.06 parts by weight of $KMnO_4$ correspond to 200.35 parts of calcium, or 3.16 grams of $KMnO_4$, N/10 dissolved in a liter volume will have a value of 1 c.c. equals 0.002 gram of calcium.

CHAPTER XVIII

PART II

THE ANALYSIS OF OPEN-HEARTH BOTTOM SAND AND FIRE-BRICK

THE sample is ground to the fineness of flour in an agate mortar. It is then dried for one hour at a temperature of 105° to 110° C. While the dried sample is still warm, it is put into a clean, dry glass-stoppered bottle, where it is cooled before using. One gram and, for a check, 0.9 gram are taken for the analysis, being weighed into 30 c.c. platinum crucibles together with 10 grams of anhydrous sodium carbonate. This flux is well mixed with the sample by stirring it with a wire. The thorough mixture of sample and carbonate is heated gradually to redness and kept at a bright red heat until the mass in the crucible, which should be in a molten state, is in quiet fusion, that is, with no bubbles of CO_2 escaping.

The melt is then cooled, and the crucible and contents are placed in a platinum dish, containing about 100 c.c. of water which is kept just below boiling until the fusion is dissolved, leaving only a stain in the crucible and a floating mass in the dish which should be free from grit. The dissolved fusion is then transferred to a 600 c.c. casserole and acidulated with 50 c.c. of conc. HCl, keeping the casserole covered with a watch glass during the very gradual addition of the acid. (In case a platinum dish is not at hand, dissolve the fusion in a casserole, in an excess of 1 : 1 HCl.)

The crucible in which the fusion was made is warmed with 5 c.c. of 1 : 1 HCl in it, to dissolve the traces of iron that still adhere to its inner walls. These cleanings are added to the main part in the casserole which is now warmed with the cover on until the carbon dioxide is mainly expelled. The watch glass cover of the casserole is rinsed off and evaporation to dryness follows. To render the silicic acid insoluble, the dry residue in the casserole is given a further heating at a temperature of about 120° C. for an hour. Care should be taken not to exceed this temperature to avoid the possibility of loss of iron by volatilization of its chloride.

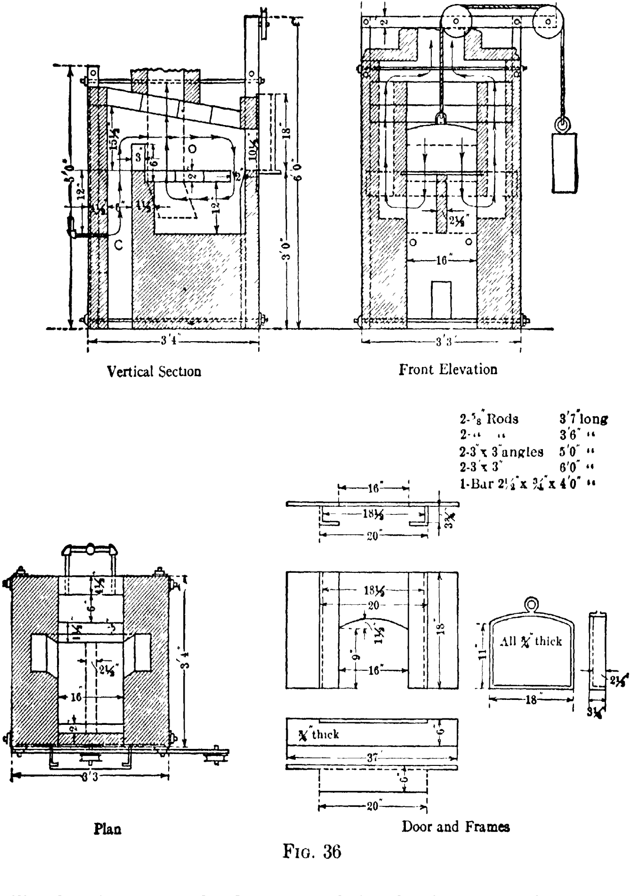
The thoroughly baked residue is cooled; moistened with conc. HCl, using about 20 c.c. of the acid, to dissolve the oxides of iron and aluminum; heated with the cover on to insure complete solution of the oxides; warmed with 200 c.c. of distilled water for a half hour with frequent stirring to secure as nearly as possible a perfect extraction of the large quantity of sodium chloride formed. Ashless filter pulp is added to the extraction, after it has been cooled, and stirred in with the now insoluble silicic acid. The mixture of pulp and silicic acid is poured on a double 15 cm. filter, that is, on to a filter consisting of two papers folded together. Such a filter will invariably secure more rapid and perfect filtration in the long run than a single filter.

The pulp and precipitate are washed, alternately, with water and 1 : 20 HCl until the washings are free from iron test, no longer giving a reddish tint with potassium sulphocyanate solution. Then the washing is continued with cold water until a few drops of the washings yield no white turbidity when tested with a water solution of silver nitrate. The filters and pulp are then removed to an air bath and dried at 120° C. until most of the water is gone. The filtrate and washings are evaporated to dryness, warmed with acid, leached with water, filtered, washed free of iron and chlorides, as before, to obtain that part of the silicic acid that may have escaped complete dehydration in the first evaporation.

The filtrate and washings from this second filtration are retained for the main part of the iron, aluminum, calcium, and magnesium. This filtrate and washings for reference are designated as A. The residues on the filters from the first and second evaporations, after having been freed from the excessive amount of wash water retained by the pulp, by drying in the air bath, are placed in as large a platinum crucible as is available and the volatile matter in the paper is smoked off, cautiously. The crucible is then brought slowly to redness and the heating is continued until the ash in the crucible is pure white. The blast is applied for ten minutes, the crucible is cooled in the air for a moment, and placed in a desiccator until entirely cold, when it is weighed. The crucible is blasted again, cooled, and weighed until a weight is obtained that does not differ from the last weight more than 0.0002 gram. This weight is taken as the final weight of the total silica together with a few milligrams of the Ca, Mg, Fe, Al, Ti, and a little of the sodium salts that cannot be entirely washed out. The true silica is then gotten by the loss of weight by volatilization with about 20 c.c. of hydrofluoric acid and 10 drops of conc. sulphuric acid, as in steels. The HF is added a little at a time to prevent loss by too violent escape of the silicon fluoride. The evaporation is carried on in a good draught until thick fumes of the sulphuric anhydride appear. It is advisable to evaporate off the HF in a specially prepared place to prevent the etching of the hood windows. Such an arrangement can be built in a wide chimney in the form of an arched space. The author places therein a large agateware pan filled with a layer of graphite. To provide a clean spot on which to stand each crucible a number of nickel disks or lids of nickel crucibles are arranged on top of the graphite. The pan is heated with a Bunsen burner. About two feet above the pan, supported by offsets in the brickwork, is a hard asbestos board one-quarter inch thick, which entirely prevents any foreign matter from falling into the open crucibles during the evaporations. A still better plan is to construct a small reverberatory furnace, lining it with asbestos board, heating it from above by a flame behind a bridge wall. Of course such a furnace is never allowed to get above a drying heat for these evaporations. Fig. 36 shows the construction of such a furnace, which with natural gas and compressed air can be brought to 1300° C., or can be kept at a mere desiccating heat by burning a small yellow flame in the combustion chamber *C*.

When the fumes of sulphuric anhydride no longer appear, the crucible is removed from the drying chamber and heated to low redness only, in order to drive off any remaining sulphuric acid, and yet not hot enough to volatilize any sodium salts that may have contaminated the silica and remained behind after the latter was evaporated away as fluoride. The crucible is then cooled in the usual way by placing it, while it is still warm, in a desiccator and then weighing it when cold. This weight is deducted from the previous weight of the crucible and its contents obtained by blasting to a constant weight. The difference so obtained is calculated to percentage as silica.

If the analyst wishes to be entirely certain that all of the silica has been completely removed, he should repeat the evaporation with HF, using but 10 c.c. of the acid and also 10 drops of the H_2SO_4. If the crucible does not lose any weight on the second evaporation and ignition then the operator has proved



Vertical Section

Front Elevation

Plan

Door and Frames

FIG. 36

the work. As previously stated, the residue in the crucible, after these evaporations, may contain traces of all of the elements present in the sand except silica. Therefore, the residue is fused with twenty times its weight of the sodium carbonate and is dissolved out as in the original main sodium carbonate fusion of the sample, and the acidulated fusion and the cleanings of the crucible are added to filtrate A which will now contain the total Ca, Mg, Al, Fe, and Ti in the sand or brick.

Filtrate A is now evaporated to 350 c.c., heated to nearly boiling and filtered; 1 : 1 ammonia is added to it until it smells slightly but distinctly of ammonia. Much excess of ammonia will prevent a part of the aluminum hydroxide from precipitating. To avoid the tedium of long boiling, add the slightest possible excess of ammonia. If the solution smells strongly of ammonia, then the excess of the latter should be neutralized with some HCl. Having the conditions of alkalinity just right, the solution is boiled for five minutes, the beaker is removed from the fire and some paper pulp is stirred in, in large or small quantity according as the precipitate seems large or small. The precipitate, which will contain all of the Fe, Al, Ti, and P in the sample, is filtered off on a double filter and washed with a solution consisting of 5 grams of ammonium nitrate dissolved in 500 c.c. of water. This is continued until the washings do not give the test for chlorides with silver nitrate. The precipitate is dissolved off the filter with hot HCl and reprecipitated as before with ammonia; filtered, and washed. The second precipitate is burned off and blasted to a constant weight as in the case of the silica. The weight obtained is recorded as Fe_2O_3, Al_2O_3, TiO_2.

The combined oxides are then dissolved by prolonged heating with conc. HCl, and if any white, floating residue remains insoluble it is filtered out; washed thoroughly in the same way as the main silicic acid, weighed, deducted from the total weight of the iron oxide, etc., and added to the total silica. The filtrate from this milligram or two of silica is reduced with stannous chloride and the iron titrated with the dilute potassium dichromate, page 442, or converted to sulphate and passed through the reductor (page 365), to obtain the amount of iron present. The latter is then calculated to ferrous oxide, FeO. It is also calculated to Fe_2O_3 and deducted from the total oxides of iron, alumina, etc. The remainder is calculated to percentage as oxides of Al, etc. (Al_2O_3, TiO_2, etc.).

The filtrates and washings from the two precipitations of the iron and aluminum are analyzed for lime and magnesia exactly as directed for limestone, beginning at the point where the combined filtrates from the double precipitations of the iron are combined, heated to boiling, and the calcium is precipitated with a saturated solution of ammonium oxalate, the only difference being that the lime content is only a per cent or two so that but 25 c.c. of the ammonium oxalate are used to precipitate the calcium present.

The ignition loss is obtained by blasting 1 gram of the sample to a constant weight. The first weight is taken after ten minutes' blasting. The sample is then blasted for five-minute intervals, until it either no longer loses more than 0.0002 gram or begins to gain weight.

When analyzing sand or brick, blanks should be run including the fusing of 20 grams of the carbonate of sodium and the putting of the solution of this melt through every operation. The iron, silica, etc., so found should be deducted from that found in the sample. There is almost certain to be some iron and silica obtained from the chemicals and glassware.

Some Analyses of Sands	No 1	No 2	No 3	No 4.	No 5.
c	%	%	%	%	%
Ignition loss	0 40	0.47	1.20	0.64	. . . . .
Silica	98.08	95 86	94.00	96.86	95.86
Oxides of iron, aluminum, etc. . . .	1.37	2.84	4.4	2.22	4.86
Calcium oxide	. . . .	. . . . .	0.15	0.38	. . . . .

Sand No. 1 is not suitable for open hearth bottoms, as it does not bond well with the bottom but floats into the slag and, as a result, the steel bath cuts through the bottom in places. No. 3 is a good sand as it contains just about the right amount of oxides of iron, etc., to bond well. No. 5 should also be a good bottom sand.

TITANIUM

Titanium is a frequent constituent of fire-brick. The best way to determine this element is to obtain the *total* iron and aluminum from a separate 1-gram portion. The hydrochloric solution of this iron, etc., is then fumed with 60 c.c. of 1 : 3

sulphuric acid and this residue is then analyzed as given for titanium either by color or gravimetrically as in steels.

ANALYSES OF MAGNESITE BRICKS

	Good Brick.	Poor Brick.
	Per Cent	Per Cent.
SiO_2	3 28	5 81
Fe_2O_3	4 71	10 85
Al_2O_3	0 52	1 39
CaO	2 59	2 76
MgO	89 15	78.84

CHAPTER XVIII

PART III

THE ANALYSIS OF IRON ORE

Metallic Iron.—Dissolve 0.400 and 0.500 gram of the floured sample (dried at 105° C.) with mild heating in 40 c.c. of conc. HCl until the insoluble residue is white and floating and free from any dark-colored grit. When the insoluble portion shows no further change, the total sample is transferred to a porcelain dish and evaporated to dryness, in case the insoluble part is not pure white. This evaporation must be done under mild heat to insure against volatilization of iron chloride. Redissolve with 20 c.c. of conc. HCl, using heat and keeping the dish covered. Add 50 c.c. of water, stir in a little ashless paper pulp, filter, wash with dilute HCl until the washings are free of iron test with KCNS. The filtrate and washings will contain all of the iron if the residue is pure white before the evaporation; but if it is the least bit colored there is possibility of it retaining some of the iron. It is at all times advisable, for close work, to burn the paper off until all black due to carbon is gone and then fuse the ash with twenty times its weight of sodium carbonate at a bright red heat for a half hour. This renders all of the iron, in the shape of silicate or titanate, soluble in HCl. The fusion is then dissolved out with a little water, an excess of HCl is added, and the solution is evaporated again to dryness, redissolved, filtered, and washed exactly as described for the original main sample. This filtrate and washings will contain all of the iron, if any, that remained in the original insoluble portion; it is added to the first main filtrate and washings obtained after the first evaporation to dryness. These combined filtrates and washings are concentrated to 200 c.c. and heated to nearly boiling in a beaker. Stannous chloride is added a drop at a time, with stirring, until the hot solution is water white, and then not more than 2 or 3 drops in excess. Place the 600 c.c. beakers in cold water until room temperature is attained. Then as each test is about to be titrated, add to it 40 c.c. of mercuric chloride solution and stir well. This should produce a silky white precipitate of mercurous chloride, taking care of the excess of the tin chloride. It is undesirable to have a large excess of the tin chloride, as there is danger of producing a gray precipitate of metallic mercury which renders the titration inaccurate; and again a huge precipitate of mercurous chloride is undesirable.

The solution being properly reduced, it is titrated with a standard solution of recrystallized potassium dichromate, until two or three drops of the solution of the ore no longer give a blue spot, test with the ferricyanide indicator but an orange color, instead.

REDUCTION BY METALLIC ZINC AND TITRATION WITH POTASSIUM PERMANGANATE*

After getting the ore in perfect solution by any of the foregoing means, the solution is converted to sulphates by evaporation to thick white fumes with 80 c.c. of 1 : 1 H_2SO_4. The iron sulphate is then dissolved again by heating to boiling for some time with 100 c.c. of water. The solution is transferred to an 800 c.c. cone flask and diluted to 200 c.c. A stream of CO_2 is passed through the flask. A total of 40 grams of zinc are added in portions to reduce the ferric iron. Heat, when the action of the zinc becomes slow, and continue to pass the CO_2 until the zinc is all dissolved. Cool to room temperature with the CO_2 passing. The CO_2 is purified by passing through two wash bottles as illustrated on page 359, photo No. 30.

A blank of the same amounts of sulphuric acid and zinc should be run. In a blank the action, toward the last, is very slow, and when there remains only about 0.5 gram of zinc, undissolved, the heat can be shut off and the solution cooled; a stopper is placed rather loosely in the flask and the latter is then let stand at room temperature until the next day, when the zinc will have completely dissolved and the blank can be titrated and deducted. The iron can be reduced with aluminum as described for uranium on page 359.

Use of the Reductor.—The most convenient way to reduce the ferric solution is by use of the well-known Jones reductor.

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* 3.16 gram $KMnO_4$ to one liter of distilled water: 1 c.c. = about 0.00556 gram Fe.

The sulphate solution of the iron is passed through the reductor at a standard speed which must be rather slow. The operator should determine the speed in drops per minute by passing a solution of a standard ore through the apparatus at the speed and volume that will give the iron value per c.c. for c.p. permanganate of potassium. See page 365 for further details concerning the reductor. (See also page 366.)

In these titrations the end-point is taken as the first pink color that spreads entirely through the solution and lasts but a few seconds.

The permanganate can be standardized by putting a similar weight of the "Sibley" iron ore standard through all of the operations, or with sodium oxalate, page 20 (1) or with oxalic acid, as given on page 405. (See also page 360.)

(1) It would seem convenient, at this point, to give the reactions involved in the method.

(2) *The reaction between the ferrous iron and the dichromate* proceeds as follows:

$$K_2Cr_2O_7+6FeCl_2+14HCl=2KCl+2CrCl_3+6FeCl_3+7H_2O.$$

(3) The following equation explains the reduction of the ferric chloride by the stannous chloride:

$$SnCl_2+2FeCl_3=2FeCl_2+SnCl_4.$$

(4) The excess of the stannous chloride is prevented from interfering with (2) by the mercuric chloride reacting to form mercurous chloride:

$$SnCl_2+2HgCl_2=Hg_2Cl_2+SnCl_4.$$

(5) If too great an excess of the stannous chloride is present, a gray precipitate of metallic mercury is produced which renders the titration inaccurate and the analysis must be repeated on a new portion:

$$Hg_2Cl_2+SnCl_2=SnCl_4+2Hg.$$

Standard and Solutions.—*The dichromate* is made by dissolving 4.9 grams of the recrystallized salt in water and diluting to 1 liter.

The stannous chloride is made by dissolving 12.5 grams of granulated tin in 125 c.c. of conc. HCl or 20 grams of the stannous salt in 100 c.c. of the conc. HCl.

The mercuric chloride consists of 50 grams of the salt dissolved in 1 liter of water.

The ferricyanide for the spot test has a concentration of 0.5 gram per 100 c.c. of water and should be made as used.

Standardization.—The standardization is best effected by putting 0.3 and 0.4 gram of the U. S. standard "Sibley" iron ore, or some other ore that has been standardized with equal care (this latter standard is very convenient in that it is entirely soluble in HCl), through all of the foregoing operations and noting how many cubic centimeters of the dichromate standard are required to oxidize the known amounts of the iron standard. By so doing, an average value, for example, of 1 c.c. of the standard equals 0.00546 gram of metallic iron was obtained.

Manganese.—Dissolve 0.100 and 0.050 gram of the powdered ore in 25 c.c. of conc. HCl. For close work filter out any insoluble matter, wash it and fuse as described under the determination of metallic iron. Dissolve out the fusion; acidulate it with HCl and add this now completely decomposed residue to the main solution; add to the latter 20 c.c. of 1 : 1 H_2SO_4 and evaporate to thick fumes; cool; add 20 c.c. of conc. nitric acid and 20 c.c. of water and heat until all of the iron and manganese sulphates are dissolved and nothing remains but the floating silicic acid. Then transfer from the porcelain dish to a cone flask, or a 10×1 inch test tube, rinsing with 1.20 nitric acid, and finish as in steels. (See page 338.)

If the manganese exceeds 2 per cent, 1.0 and 0.9 gram are gotten into solution as above and the analysis can be finished by the phosphate method or by the method given on pages 345 to 347. (See also pages 250–252.)

Phosphorus and Silica.—Dissolve 0.9 and 1.00 gram, as for the metallic iron, using 40 c.c. of conc. HCl, fusing the insoluble residue and placing the acidulated melt back in the main solution; then evaporate to dryness; adding 1 gram of chlorate of potassium before evaporating, heating with the cover on the porcelain dish until all action caused by the addition of the chlorate is over. After the evaporation to dryness, redissolve in 20 c.c. of conc. HCl; evaporate to 10 c.c., add 20 c.c. of water; add a little ashless filter pulp; filter and wash with 1 : 40 HCl until the washings no longer give an iron test with KCNS; evaporate the filtrate and washings again to dryness on the graphite, dissolve, dilute, filter and wash as before to insure the separation of all of the silica. The filters from the first and second evaporations to dryness contain the total silica. These papers are ignited, weighed, and finished for silica, purifying with $HF+H_2SO_4$.

The filtrate from the second filtration and washing contains all of the phosphorus; it is evaporated low and is converted to nitrates, boiled with permanganate, and finished for phosphorus as in steel (pages 310 and 318).

Sulphur.—Fuse 1.0 and 0.9 gram, as given for ferro-titanium at the bottom of pages 47–48; running blanks as a check on the reagents. (See also page 122.)

Aluminum, Calcium, and Magnesium.—Get 0.9 or 1.0 gram into solution and evaporate to dryness as for silica. The filtrate from the second evaporation will contain all of the aluminum, iron, manganese, most of the titanium, all of the phosphorus, calcium, and magnesium. Make a double basic acetate precipitation of the filtrate as described on pages 250 and 251 and combine the two sets of filtrates and washings for the calcium and magnesium. The precipitate from the second basic acetate precipitation is burned off at a low heat, blasted to constant weight, and weighed as Al_2O_3, Fe_2O_3, TiO_2, P_2O_5. The residue in the crucible is then dissolved in conc. HCl and divided into two parts; the phosphorus is determined in the one part after converting it into nitrate as described under phosphorus; and in the other part the metallic iron is found as given under metallic iron, by reducing this half with stannous chloride or convert to sulphate and use the reductor. The iron so found is calculated to Fe_2O_3, multiplied by two and deducted from the total weight of the oxides. In the same way the phosphorus found is calculated to P_2O_5, multiplied by two and deducted. This leaves only the weight of the Al_2O_3 and TiO_2. The latter is determined on a separate portion and calculated to a 1-gram basis and deducted, leaving the aluminum only.

Also these same weights of ore can be gotten into solution as for silica, the silica filtered off; the filtrate and washings therefrom can be transferred to a 1 liter boiling flask and the iron, manganese, and titanium can be removed by two or three peroxidations. The filtrates and washings from peroxidations can then be made acid and the aluminum precipitated at once with ammonia; redissolved and reprecipitated to remove the sodium salts that are inevitably present in the aluminum hydroxide. The reprecipitated aluminum hydroxide is weighed as Al_2O_3, P_2O_5. The phosphoric anhydride is determined by fusing the two oxides in twenty times their weight of anhydrous sodium carbonate; the melt is dissolved in nitric acid and is then evaporated to 40 c.c. and finished as in steels, pages 310 and 318.

This latter scheme is decidedly to be preferred if calcium and magnesium are not needed.

Calcium and Magnesium.—The filtrates from the two basic acetate precipitations are combined and evaporated nearly to crystallization with 100 c.c. of conc. HCl. Then 200 c.c. of water, or more, are added and heat is applied until the salts are all dissolved. If any dirt or dust has crept into the solution the same is filtered out and the filtrate and washings are finished for Ca and Mg as in limestone from the point where the filtrates from the iron have been obtained and are ready for the addition of the oxalate. (See page 431.)

Also, if it is desired to obtain the latter elements in a separate portion one can proceed exactly as given for limestone (page 430).

Titanium.—Fuse 1 gram with 20 grams of acid potassium sulphate and finish for titanium as directed on page 49, ("Transfer to an 800 c.c. beaker"), if the titanium content of the ore amounts to more than 1 per cent. If the per cent of titanium is less than 1 per cent, fuse as above but boil the sulphuric acid solution of the fusion obtained as directed on page 61 with strong nitric acid and compare it with an iron ore, containing a known amount of titanium, that has been put through all of the operations. Dilute the sulphuric acid solution of the fusion to 100 c.c.; boil it five minutes with 25 c.c. of conc. nitric; cool and compare as given for steels on page 64.

Copper and Nickel.—Dissolve the ore as far as possible with HCl, using 20 c.c. of the conc. acid per gram, heating a little below boiling in an 800 c.c. beaker until the insoluble residue does not show any further change, that is, does not become any whiter. Use 15 grams of the finely ground sample if the copper and nickel do not exceed 1 per cent. When the HCl is apparently having no further effect, then add cautiously 10 c.c. of conc. nitric per gram of ore taken and also a total of 10 c.c. of hydrofluoric acid and digest the contents of the beaker for at least one hour.

Evaporate to moist dryness, but do not bake for fear of rendering the nickel insoluble; redissolve in 100 c.c. of HCl and evaporate until the solution does not seem to have a great excess of HCl; convert the solution to nitrate by evaporating until further additions of conc. nitric acid no longer produce red fumes, or until a few drops of the solution give but little, if any, milkiness with silver nitrate solution. Then finish for copper and nickel as given on pages 210 to 212. Run as a standard an iron ore containing a known amount of copper, or if such a standard is not at hand, then add to the ore a known amount of copper and nickel and also run the same ore without any copper and nickel, performing the standardization in the same way as given for pig iron on pages 206 and 207.

Chromium.—Determine the chromium exactly as given for chrome ore on pages 184 and 185.

Ignition Loss, Carbon Dioxide, and Moisture.—The ignition loss is obtained by heating 1 gram of the sample at a bright red heat for an hour.

Carbon dioxide and organic matter can be determined together as CO_2 by burning 1 gram of the sample in the electric combustion furnace for one hour in a stream of oxygen as in steels. The CO_2 existing as such can be determined by heating the ore with conc. HCl in a flask through which a constant stream of air is drawn and purified from CO_2 in the same manner as the oxygen is purified for the determination of carbon in steel. The flask should be provided with a No. 6 rubber stopper. The flask shown for sulphur work on pages 330 and 332 will answer. The stopper should be pierced with a funnel tube as shown on page 332; also an inlet tube for the purified air which should extend one-quarter inch below the acid in the flask; the stopper must also have an outlet tube extending through the stopper into the flask, but not touching the fluid in the same. This tube will conduct away the CO_2 liberated by the digestion with HCl by means of gentle suction with a water pump connected to the outlet of the weighing apparatus. The weighing apparatus and the train between it and the outlet of the digesting flask can be made exactly as the same part of the carbon combustion apparatus. The whole apparatus can be thought of as parallel to the carbon outfit with the flask taking the place of the electric furnace. If it is more convenient oxygen can be forced through the apparatus, during the digesting period, instead of drawing air through the outfit. The weighing apparatus *J*, page 279, should be weighed after air or oxygen has been drawn through it during an hour's digestion. *J* is again attached and air passed through it for another half hour, but during this second passage of the air, or oxygen, no heating should be necessary. If there is no more gain of weight than a blank gives at this point, then it is proven that all of the CO_2 has been drawn over into the weighing apparatus. The operator can check his apparatus and the accuracy of his manipulations by determining the CO_2 in limestone containing a known amount of calcium carbonate or by taking a known weight of calcite crystals.

The moisture is determined by weighing 1 gram of the sample and drying it to a constant weight at 105° C.

Combined water is determined as in an unburned crucible, page 398, using 1 gram of the sample that has been already dried for one hour at 105° C. and kept in a glass-stoppered bottle after the drying.

Vanadium is determined in the same manner as given for carnotite ore, page 369.

CHAPTER XVIII

PART IV

THE ANALYSIS OF FLUORSPAR

Exact Method.—As this mineral is not completely decomposed by fusion with sodium carbonate alone, it is the general practice to fuse the finely ground mineral with a mixture of sodium and potassium carbonates, and finely ground precipitated silica. The author uses, for the melt, an intimate mixture of 1 gram of the sample with 10 grams each, of the two carbonates mentioned, together with 3 grams of precipitated silica.

The 1 gram of the spar is stirred carefully through the flux in a thirty-gram platinum crucible and the whole is gradually brought to a bright red heat and held at this temperature until all bubbling due to the evolution of CO_2 ceases, indicating that the reactions are complete as follows:

$$3CaF_2+3SiO_2=CaSiF_6+2CaSiO_3, \quad . \quad . \quad . \quad . \quad (1)$$

$$CaSiF_6+4Na_2CO_3=CaCO_3+Na_2SiO_3+6NaF+3CO_2. \quad . \quad (2)$$

When the fusion is finished in the manner indicated, it is run around the sides of the crucible; and, when cooled, the crucible is placed in a platinum dish and its contents dissolved in water with heat. If no platinum dish is available, then the melt *must* be dissolved in the cold in a porcelain dish. When all is dissolved except the floating portion, cool, add paper pulp, filter into a large casserole and wash the residue on the filter with 2 grams of sodium carbonate dissolved in 500 c.c. of water, giving the filter at least fifty washings, obtaining residue *R* on the filter, and the filtrate and the washings *A*, which latter will contain all, or nearly all, of the fluorine as NaF and much silicic acid as sodium silicate, according to (2).

The main silica in filtrate *A* is separated according to the method of Berzelius, by heating with ammonium carbonate and removing the last traces with an ammoniacal solution of zinc oxide as follows: 20 grams of ammonium carbonate, in powdered form, are added to *A* and the same is heated for an hour at 40° C. *A* is then filtered after twelve hours. Considerable ashless filter pulp is stirred in with the precipitated silicic acid. The mixture of pulp, silicic acid and perhaps some iron and aluminum hydroxides is filtered out and washed with one gram of ammonium carbonate dissolved in 500 c.c. of water, at least fifty times, allowing each washing to drain off completely before the next one is applied. This filtrate and washings can be designated as *B* and contain the major part of the sodium fluoride and still some of silicic acid. The mixture of pulp and silicic acid on the filter from *A* can be marked *M*.

The residues *R* and *M* are smoked off in a large platinum crucible and then the heat is raised until the ash is free of charcoal and of a light-brown color. In this way nearly all of the original added silica is returned to aid in attacking any undecomposed spar that may have escaped decomposition in the original fusion. Place on top of the ash from *R* plus *M* a ground mixture of 10 grams, each, of the carbonates of sodium and potassium. Stir this flux all through the ash *R* plus *M* with a stout ni-chrome wire and then repeat the fusion as described in the first place, and all of the other foregoing operations. The water-insoluble residue *R'* from the second fusion is washed with sodium carbonate water as in the case of *R*. This water-insoluble residue *R'* contains all of the calcium, barium, magnesium, iron, and some of the aluminum. The filtrate and washings from *R'* contain any remainder of the fluorine and nearly all of the silicic acid and aluminum (if Al be present). This filtrate and washings are heated with ammonium carbonate as in *A*, allowed to stand for some hours, filtered, washed with ammonium carbonate water, obtaining a residue *M'* on the filter consisting of nearly all of the silicic acid plus a little iron and aluminum. The filtrate and washings from *M'*, i.e., *B'*, contain the last traces of the silica. This filtrate combined with *B* contains all of the fluorine as sodium fluoride and the remainder of the silica as sodium silicate. This silica is removed as follows: Evaporate these filtrates to dryness in a casserole; take up with as little water as possible; add a few drops of an alcoholic solution of phenolphthalein and then add 1 : 1 HCl until a few drops of this acid just discharge all pink color. The solution is then boiled to note if the pink color may reappear, and if it should, a drop or two more of the acid is added to just remove the pink and so on until no pink reappears on heating. The solution will then be neutral and is ready for the removal of the last traces of the silicic acid by means of a saturated solution of zinc oxide in ammonia, prepared as follows: Dissolve 10 grams of zinc oxide in 50 c.c. of conc. ammonia and filter off the undissolved zinc oxide. Add 10 or 12 c.c. of this filtrate to the neutralized *B* plus *B'* to precipitate the silicious matter still remaining therein, as zinc silicate. After adding the ammoniacal zinc solution, boil until the smell of ammonia is gone, and then filter out the mixture of zinc silicate and zinc oxide and wash it with 5 c.c. of the ammoniacal solution of zinc oxide diluted with 500 c.c. of water, obtaining filtrate and washings *C* which contain all of the fluorine as sodium fluoride and free of silica. The silicic acid gotten from *B* plus *B'* as zinc silicate is freed from zinc by dissolving it off the filter with nitric acid, 1.20, and evaporating the filtrate and washings so obtained to dryness. The dry residue is taken up with 1.20 nitric acid and filtered off, after dilution with water, on the same filter from which the zinc silicate was dissolved with nitric acid. The residue on this filter is washed thoroughly and burned off with *M'*.

The Calcium Fluoride.—The filtrate *C* is heated to boiling and the fluorine is precipitated from it while boiling by means of a saturated solution of calcium chloride. Some recommend the addition of a little sodium carbonate before adding the precipitant, thus causing a precipitation of some calcium carbonate along with the calcium fluoride to aid in the subsequent filtration. The calcium fluoride is filtered and washed thoroughly with water. It has been the writer's experience that it requires not less than fifty washings to completely wash a large precipitate. The CaF_2 is burnt off in a platinum crucible at a very low heat, just smoking off the paper, and then at low red to remove the carbon.

The ash, which consists of a mixture of oxide, fluoride and carbonate of calcium, is dissolved with dilute acetic acid (three parts of the acetic acid diluted with 1 part of water), by heating and evaporation to dryness on the water bath. The calcium fluoride remains insoluble and the calcium carbonate and oxide are dissolved. After the evaporation to dryness, 50 c.c. of water are added to the dry residue and heat is applied for about a half hour. The insoluble calcium fluoride is filtered off and washed with water, dried, ignited at a low heat and finally at redness until the CaF_2 is white, when it is cooled and weighed and calculated to percentage as such. As a check on the purity of the CaF_2 it is evaporated to dryness with 5 c.c. of conc. H_2SO_4. The excess of sulphuric acid is driven off at a low red heat and the residue is weighed as calcium sulphate, 1.7437 grams of which equal 1 gram of calcium fluoride.

Silica.—The water-insoluble residue R' is smoked off in a platinum crucible and then heated at redness until all carbon from the paper is gone. The ash which contains the main calcium, etc., is transferred to a porcelain dish and boiled for a few minutes with 30 c.c. of 1 : 1 HCl until all but perhaps a little silica is dissolved. The latter is filtered off, washed, designated as M'' and burned with M'. The ash from the burning of M' plus M'' contains the total silica, that is, the silica that was added plus that contained in the sample. The total silica is then evaporated as usual with an excess of HF plus 5 drops of conc. H_2SO_4. The HF should be added very cautiously, and in small instalments, to prevent loss by spraying during the formation of the volatile silicon fluoride. The silica is then determined by the loss of weight after the removal of the excess of the two acids as in steels. Any residue remaining in the crucible after the removal of the silica may contain some calcium, iron, etc., and is fused with a little sodium carbonate, dissolved in HCl and added to the filtrate from M''.

Ca, Mg, Ba, Fe, and Al are now all in solution in the filtrate just mentioned. The first step is to remove any barium present by adding to the solution 2 c.c. of conc. sulphuric acid diluted with 600 c.c. of water. Any precipitate formed by the addition of the very dilute sulphuric acid is filtered off, ignited and weighed as barium sulphate. The filtrate and washings from the barium sulphate are then analyzed for Ca, Mg, iron, and aluminum as described for limestone, beginning at the point where these elements are all in solution and free of silica. (See page 431.)

Blanks.—It is very necessary to run blanks by fusing 3 grams of the same lot of precipitated silica as used in the decomposition of the spar with 10 grams, each, of the sodium and potassium carbonates. The melt is dissolved out in water and then put through all of the operations given in the method. The silica, iron, calcium, magnesium, and aluminum so found are deducted from the amounts of these elements found in the analysis of the sample. These blank analyses should be made in duplicate, as should the analysis of the spar, also.

Lead.—Dissolve 0.9 and 1.0 gram of the sample in a mixture of 20 c.c. of conc. HNO_3 and 10 c.c. of conc. HCl. If the spar is high in CaF_2 it will dissolve almost completely in this mixture. Heat until all spraying is over and evaporate to moist dryness; redissolve in 20 c.c. of conc. nitric acid, dilute, filter, wash with dilute nitric acid, and evaporate the filtrate and washings to 10 c.c. Add 75 c.c. of conc. HCl and evaporate to 15 c.c. Dilute with water to about 100 c.c. Make the diluted solution just neutral with ammonia; add 4 drops of HCl and pass H_2S through the hot solution until the black precipitate of lead sulphide settles well. Filter off the lead sulphide and wash it with H_2S water. Pass H_2S through the filtrate and washings to make certain that all of the lead has been precipitated. The lead sulphide is dissolved in 50 c.c. of 1.20 nitric acid and its solution is evaporated to heavy fumes with 75 c.c. of 1 : 3 sulphuric acid, in a porcelain dish. Cool, dissolve as far as possible with 200 c.c. of water and one-third this amount of alcohol. Allow the lead sulphate to settle for several hours before filtering; filter off the lead sulphate and wash it with a mixture of 2 parts of water and 1 part alcohol. Burn the residue at a very low heat in a *porcelain* crucible until the paper is all gone. Cool the white residue and moisten it with a drop or two of H_2SO_4 and ignite the residue again at a dull red heat.

The weight so obtained is multiplied by 0.6832 to reduce to the metallic basis. If the sulphur found is reported as such then the lead can be conveniently reported as metal. The lead, however, usually is present as the sulphide.

Sulphur.—The author uses the carbonate and niter fusion, melting the spar with 20 grams of carbonate of soda and 4 grams of niter. The analysis is then finished as in ferro-vanadium high in silicon (see page 34 near the bottom of the page). There is no reason why the sulphur could not be obtained by fusing the mineral in a mixture of 10 grams of sodium peroxide and 5 grams of sodium carbonate, then dissolving out the melt in water. The water solution could be acidulated with a considerable excess of HCl and the analysis finished as in the carbonate and niter fusion.

In either method blanks should be run through all the operations and deducted.

Carbon Dioxide.—Ignite 1 gram of the sample in the electric combustion furnace in a stream of oxygen for one hour, as in the determination of carbon in steel. The carbon dioxide is usually combined with calcium, as carbonate, in the mineral.

Approximate Method.—The usual approximate method is to attack the spar with acetic acid. The author proceeds as follows (he regards the approximate method accurate enough for all technical purposes): Moisten the finely ground spar to a thin paste with water, add 20 c.c. of glacial acetic acid and evaporate to dryness on the water bath in a porcelain dish. To the dry residue add 50 c.c. of water; stir; boil a few minutes; add ashless paper pulp; mix again, filter, and wash with hot water, obtaining residue *R* on the filter and filtrate and washings *F*. The residue *R* contains all of the CaF_2, silica and the main portion of the iron, aluminum and lead. Barium if present as sulphate would be mainly in *R*.

The filtrate and washings from *R* contain calcium, magnesium and some of the iron and aluminum, and are analyzed for these elements as in limestone (see page 430). If lead is present some of it will also be in this filtrate and should be first removed by H_2S precipitation of the hot, faintly acid solution. The lead sulphide is washed with H_2S water and the filtrate and washings are evaporated low to remove the excess of H_2S, adding some potassium chlorate to oxidize the iron, at the beginning of the evaporation. The amount of lead found at this point is only a small portion of the total amount of the lead present; at least, this is the case in the samples containing lead as galena.

Silica and Calcium Fluoride.—The residue *R* is ignited at a low red heat in a weighed platinum crucible, cooled and weighed. Twenty c.c. of c.p. HF are added to *R* after the weighing. Evaporation to dryness removes the silica. The remainder in the crucible is then heated to lowest redness, cooled, weighed again, and the loss of weight due to the evaporation and ignition is calculated as silica. Three c.c. of conc. H_2SO_4 are dropped into the crucible and the contents of the latter are taken to dryness; ignited at a low red heat, cooled and weighed as calcium sulphate ($CaSO_4$). The calcium sulphate so found is calculated to calcium fluoride after deducting from it any Ba, Pb, Fe, and Al found as given below.

Add 15 c.c. of conc. HCl to the weighed calcium sulphate and boil it until the sulphate either dissolves to a clear solution after twenty minutes' slow boiling, or there remains some white insoluble residue which would indicate the presence of barium sulphate. If such a residue be found, then dilute the solution to 200 c.c. and let it stand for several hours to permit the barium sulphate to settle. Filter it out; wash it with water; ignite; cool; weigh, and deduct it from the weight of the calcium sulphate. The filtrate and washings from the barium sulphate are diluted to 400 c.c. and H_2S is passed for an hour and the solution is then permitted to stand for several hours to give the precipitate of PbS time to separate out. If there be sulphide of lead in the spar (usually in the form of galena), then some of it will have been counted as calcium sulphate. The lead sulphide is burned at a very low red heat in a porcelain crucible, moistened with a few drops of conc. sulphuric acid and the latter is evaporated. The residue is burned at a low red heat, weighed and the weight is then deducted from that of the calcium sulphate. The filtrate and washings from the lead sulphide are evaporated to dryness with a gram or two of potassium chlorate and analyzed for any small amounts of iron and aluminum that may be present in this part of the analysis; that is, the small residue in the evaporating dish is dissolved in 10 c.c. of HCl, precipitated with a slight excess of ammonia, the small precipitate of iron and aluminum hydroxides are filtered out, washed, weighed, and the weight also deducted from the weight of main calcium sulphate. The main calcium sulphate as stated, after these deductions, is then calculated to the total calcium fluoride. These small portions of the Fe and Al are also added to the main oxides of iron and aluminum found in *F*. The main filtrate *F* contains all of the calcium and magnesium *not* existing in the mineral as fluorides; also the remainder of the lead if any is present and the main portion of the iron and aluminum. The lead is removed first, after acidulating *F* with a slight excess of HCl to prevent the coprecipitation of any iron, by means of hydrogen sulphide. The filtrate and washings from the lead sulphide are evaporated to dryness with an excess of at least 20 c.c. of conc. HCl and 1 gram of chlorate. The dry residue is then taken up with 10 c.c. of 1 : 1 HCl and the iron, aluminum, calcium, and magnesium in the solution are determined as in limestone. As stated, the lead, iron, and aluminum found here are added to any portions of these elements found in the filtrate from the hydrochloric solution of the calcium sulphate.

CALCULATIONS

In the *exact method*, the calcium required in the calcium fluoride found is deducted from the *total* calcium found. Any calcium remaining is usually calculated to calcium carbonate. The author prefers for the sake of simplicity to calculate to calcium oxide, the calcium found in excess of that necessary to produce the calcium fluoride; and report the carbon dioxide found, as such instead of attempting to distribute it as carbonate. In the same way the sulphur found is reported as such instead of entering into a tedious computation for the purpose of calculating a part of it to lead sulphide and any remaining sulphur to sulphide of iron. Similarly the oxides of iron and aluminum obtained are reported as oxides. For commercial and technical purposes this seems the logical procedure, and entirely answers purposes of the iron and steel metallurgist. In harmony with the reporting of the sulphur as such, the lead found is recorded as metal.

CALCULATION OF THE CALCIUM EXISTING AS CaO BY THE EXACT METHOD

Suppose that 83.46 per cent of CaF_2 were found. Then in 1 gram of the sample there would be 0.8346 gram of calcium fluoride. Further, in 1 gram of this sample there was found a total of 0.6956 gram of calcium oxide in the filtrate from *M''*, page 453; then as calcium fluoride is converted to its equivalent weight of calcium oxide by the factor of 0.7182 we have 0.8346 multiplied by 0.7182 or 0.5994 gram of calcium oxide coming from the calcium in the calcium fluoride. This is deducted from the total calcium oxide; 0.6956 minus 0.5994, or 0.0962 gram of calcium oxide to be reported as such, being 9.62 per cent.

CALCULATION OF $CaSO_4$ TO CaF_2 IN THE APPROXIMATE METHOD

The calcium sulphate found is multiplied by the factor 0.5735 to obtain the equivalent weight of calcium fluoride.

SOME ANALYSES OF FLUORSPAR

SAMPLE OF FAIRVIEW GRAVEL

	Approximate Method Per Cent	Exact Method Per Cent
Calcium fluoride	83 70	83 46
Silica	2 92	3 20
Oxides of iron and aluminum	3 16	3 20
Calcium oxide	9 40	9.61
Sulphur	0 016	0 016

SAMPLE OF FLUORSPAR GRAVEL CONTAINING SULPHIDE OF LEAD

	Approximate Method Per Cent	Exact Method Per Cent
Calcium fluoride	84 24	84 36
Silica	5 44	5 79
Oxides of iron and aluminum	1 32	1 41
Calcium oxide	1 83	1.90
Carbon dioxide	2 20	2.20
Sulphur	0 92	0 92
Metallic lead	2.00	2.00
Moisture	0 35	0 35

SELECTED SAMPLE BY THE APPROXIMATE METHOD

	Per Cent		Per Cent.
Calcium fluoride	97 58	Oxides of iron, etc.	0.77
Silica	0.20	Oxide of calcium	0.62

Evolution Method for Fluorine.—J. B. Krak in The Chemist-Analyst, July, 1914, gives the following evolution scheme: " Weigh the substance (he does not state how much, presumably 1 gram) into a 700 c.c. flask provided with a separatory funnel. Connect the flask with a condenser and a train of three Fresenius nitrogen bulbs. Pour into the dissolving flask 100 c.c. of phosphoric acid of 85 per cent strength. Add 100 c.c. of water. Close the funnel stopcock. Apply low flame and continue to heat until 100 c.c. of the solution in the flask has been distilled over (Fig. 37).

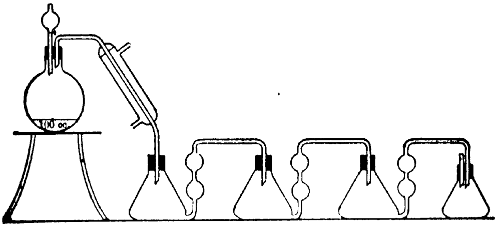

Fig 37.

Add 100 c.c. more of water and distill this over also. The nitrogen bulbs contain an absorbing solution consisting of 90 c.c. of 3 per cent calcium acetate and 5 per cent sodium acetate made acid with acetic acid. The theory is that the fluorine is absorbed as HF in the calcium acetate, forming a precipitate of CaF_2. Any silicon tetrafluoride that may be formed is also distilled over forming CaF_2 and sodium silicate. The author has never tested this method, but its simplicity leads him to publish it for those of his readers that may be interested to test its accuracy.

The contents of the nitrogen bulbs are poured out into a large beaker, 20 c.c. of a saturated solution of ammonium acetate are added, evaporation, boiling, and filtering out of the CaF_2 follow. Wash the CaF_2 with a dilute solution of ammonium acetate; ignite at a low heat, and weigh as CaF_2.

CHAPTER XIX

PART I

THE TESTING OF LUBRICATING OILS

As the steel works chemist is frequently required to report on the lubricants used about the plant, a brief outline of the more important tests may save the busy reader of this book much delving into the vast amount of literature written on this subject. The tests about to be described constitute all that the mechanical engineering department of a large works usually cares to know, or asks for. If the reader wishes to inform himself further, he can consult the writings of Lewkowitch, Benedict, Gill and others.

SAPONIFICATION NUMBER

This test is a direct index of the proportion of animal matter in the lubricant for the reason that mineral oil (usually present in most of the oils used for lubricating) has no saponification value. The saponification number simply means that 1 gram of the sample tested requires that many milligrams of potassium hydroxide to combine with (saponify) the fatty acids present in it. The test is also known as the Koettstorfer's value.

Method.—Weigh 1 to 2 grams of the oil or lubricant into a 250 c.c. conical flask. Place also in the flask 25 c.c. of half normal potassium hydroxide. Insert a stopper carrying a return condenser firmly in the neck of the flask. Turn a current of water into the condenser and start to heat the flask on a water bath. (See photo No. 38.) Some operators add 20 c.c. of ether to the contents of the flask before putting in the condenser. Heat the flask on the water bath for one hour. Then shut off the heat, turn off the water, cool, add several drops of phenolphthalein indicator and drop in from a burette half-normal HCl until the pinkish color or shade given to the solution by the indicator just disappears. The number of c.c. of N/2 KOH added, less the number of c.c. of HCl required to discharge the pinkish color produced by the KOH, multiplied by the factor 28.05 (1 c.c. N/2 KOH contains 28.05 mgs. of KOH) and divided by the weight of the oil taken gives the saponification number of the sample. In weighing the oil place the tared flask on the balance pan and drop in some of the sample from a pipette until about the desired weight has been put in the flask. Then weigh the oil exactly.

Photo 38.

When titrating the oil with N/2 HCl use alcohol to wash down the sides of the flask, as water is liable to cloud the solution. To check the operations place 25 c.c. of the N/2 KOH in the cone flask together with the 20 c.c. of ether. Connect the condenser and heat the flask for one hour in the water bath, cool and titrate with the N/2 HCl. Any KOH that may have been so used is deducted from the apparent amount used by the sample, before calculating the saponification number as given above.

A convenient standard for checking the operator's work is the purest rapeseed oil. A very pure sample obtained by the author gave a saponification value of 185. A German rape oil known as double refined was found to be 182 in saponification. Pure lard oil is given as 195. These pure oil standards should be kept in a cool dark cupboard, in sealed bottles, when not in use.

THE PREPARATION OF HALF-NORMAL (N/2) HCl AND HALF-NORMAL KOH

A normal solution is usually defined as the hydrogen gram equivalent of the active substance dissolved in a liter volume. The author would like to offer the following definition, which may seem long drawn out but more explanatory:

A normal solution is the gram molecular weight of the reacting substance dissolved in a liter volume, or that fraction of its gram molecular weight dissolved in a liter volume which is the equivalent of the gram atomic weight of hydrogen. The required fraction of the gram molecular weight may be different for the same compound, depending on the nature of the reaction for which the normal solution is to be used.

The first requisite is then to write the equation and from it decide whether the full molecular weight in grams or only a fraction of it is needed to meet the conditions of normal solution. Suppose the normal solution of permanganate of potassium is desired for the oxidation of ferrous sulphate, according to the equation:

$$\text{(A)}\quad 10FeSO_4+2KMnO_4+8H_2SO_4=5Fe_2(SO_4)_3+K_2SO_4 +2MnSO_4+8H_2O,$$

or

$$\text{(B)}\quad 10FeO\cdot SO_3+K_2O_2\cdot 2MnO_3+8H_2O\cdot SO_3=5Fe_2O_3(SO_3)_3 +K_2O\cdot SO_3+2MnO\cdot SO_3+8H_2O.$$

By equation (B) we see how the oxidation expressed by (A) takes place: The ferrous oxide united to the sulphuric radical and containing 10 atoms of oxygen becomes ferric oxide, still united to the sulphuric radical, and gains 5 atoms of oxygen. This gain comes from the permanganate as by equation (B) the potassium peroxide part of the permanganate loses 1 atom of its oxygen to the ferrous sulphate, becoming potassium sulphate; and the two parts of manganic trioxide give up 4 atoms of oxygen to the ferrous sulphate, and become 2 molecules of manganous sulphate. Hence we have permanganate equivalent to 5 atoms of divalent oxygen or 10 atoms of monavalent hydrogen; therefore 2 molecules of the permanganate being equivalent to 10 atoms of hydrogen then two-tenths or one-fifth of a gram molecule of the $KMnO_4$ will be the equivalent of the gram atom of hydrogen. This makes it necessary to weigh one-fifth of 158.03 or 31.6 grams of the $KMnO_4$, dissolving the same in a liter volume.

A normal solution of the ferrous sulphate: It has been seen that the sulphate of iron has taken up 5 atoms of oxygen which are equivalent to 10 atoms of hydrogen, hence, since 10 molecules of the ferrous sulphate are equivalent to 10 atoms of hydrogen, then 1 molecule of the sulphate is equivalent to 1 atom of hydrogen. It will be fulfilling the definition if 278 grams of $FeSO_4, 7H_2O$ are dissolved in a liter volume, or the entire gram molecule.

An example of a normal solution for a precipitation reaction is afforded by the following: $H_2SO_4+BaCl_2=BaSO_4+2HCl$. In this equation the active sulphuric acid molecule precipitates the divalent barium atom which is equivalent to 2 atoms of the monavalent hydrogen atom, therefore one-half the gram-molecular weight of the sulphuric acid, or 49.04 grams of the 100 per cent acid or its equivalent in a dilution, in a liter volume constitutes its normal solution.

(C) This brings one to the neutralization normal, or half-normal solution: $HCl+KOH=KCl+H_2O$. In this reaction whether it is desired to consider the normal solution for the potassium hydroxide or the hydrochloric acid it is an example of one molecule reacting with a monavalent atom. In either case the entire gram molecule would be required in the liter volume or one-half this amount for the half-normal solution, also in a liter volume. This would be 36.47 grams of the HCl and 56.11 grams of the KOH in a liter volume for the normal solution, or 18.23 grams of HCl and 28.05 grams of KOH dissolved in a liter volume for the half-normal solution (N/2) of these salts.

.**Half-normal HCl.**—As the hydrochloric solution will remain constant, 7 liters are prepared as follows: 350 c.c. of about 1.20 specific gravity acid are diluted to 7000 c.c. with water and well mixed. The acidity is then tested against pure sodium carbonate prepared from c.p. sodium oxalate which can be obtained to the best advantage from the U. S. Bureau of Standards.

Weigh 1 gram of the standard oxalate into a platinum crucible and gently ignite until it is charred and then raise the heat until it is pure white but do not heat it above redness. Dissolve the sodium carbonate thus formed in a little water and transfer it with great care to a 250 c.c. cone flask. Add 1 or 2 drops of methyl orange solution and titrate it with some of the above HCl solution until one drop of the acid just turns the fluid in the cone flask pink. The reaction is as follows:

$$Na_2CO_3+2HCl=2NaCl+H_2O+CO_2. \quad . \quad . \quad . \quad (2)$$

The sodium oxalate on ignition is decomposed to sodium carbonate in the manner shown by the equation,

$$Na_2C_2O_4+O=Na_2CO_3+CO_2. \quad . \quad . \quad . \quad . \quad (1)$$

By (1) one molecule of sodium oxalate yields 1 molecule of sodium carbonate and by (2) we see that 1 molecule of sodium carbonate is also equivalent to 2 molecules of hydrochloric acid. Or in terms of equivalent weights, 134 parts of sodium oxalate yield 106 parts of sodium carbonate, which require 72.94 parts of HCl (2HCl) for neutralization. One gram of sodium oxalate will give $\frac{106}{134}$ of a gram of sodium carbonate, or 0.791 gram. Suppose that the trial titration of 7 liters of HCl showed that 0.791 gram of sodium carbonate required 25.0 c.c. of this HCl to give a pink with the methyl orange. By (2) we have seen that 72.94 parts by weight of HCl unite with 106 parts of sodium carbonate or 1.4532 grams of Na_2CO_3 equal 1 gram of HCl. N/2 HCl according to (C) contains 18.23 grams of HCl to the liter, therefore 1 c.c. of N/2 HCl $=18.23\times1.4532\div1000$, grams of sodium carbonate, or 0.02650 gram of Na_2CO_3. As an average of several titrations it was found that 25 c.c. of the solution of HCl being tested neutralized 0.791 gram of Na_2CO_3, hence 1 c.c. of this acid equals 0.791 gram $\div$ 25, or 0.03164 gram of Na_2Co_3. As 1 c.c. of N/2 HCl should equal 0.02650 gram of Na_2CO_3 then 1 c.c. of the acid being tested should be diluted in volume as many times as 0.0265 is contained in 0.03164, or 1.194 times. Suppose after making the trial titrations there remains exactly 6800 c.c. of the HCl, then this solution should be diluted to 6800×1.194 c.c., or to 8119 c.c., when it should be an exact N/2 normal solution.

In general divide any number of c.c. of the acid being standardized into the amount of sodium carbonate that it will exactly neutralize; divide the result by 0.02650 and then multiply this last quotient by the exact number of c.c. of the acid remaining. This will give the volume to which the remaining acid must be diluted to make it of N/2 strength.

The Preparation of N/2 KOH.—Weigh about 40 grams of KOH, marked purified by alcohol, into a glass-stoppered bottle and dissolve it in a liter of ethyl alcohol that has been distilled with some KOH.

This distillation can be accomplished by placing the alcohol and KOH in a boiling flask, in boiling water and connecting the same with a Bunsen condenser. The distillate is then used as above. In the alcoholic solution a gram or two of barium hydroxide are also placed to remove any carbonate present in the KOH solution. It is then allowed to settle for twelve hours, when the clear liquid is siphoned off, leaving all of the cloudy portion behind. This clear portion is diluted to one liter and well mixed in a glass-stoppered volumetric flask. The redistilled alcohol is used for this dilution also. Exactly 50 c.c. of this KOH are withdrawn from the 1000 c.c., and 25 c.c. of it are titrated with the N/2 HCl. Suppose it is found that 28.7 c.c. of the N/2 HCl are required to just turn the 25 c.c. of the KOH pink; then 1 c.c. of the KOH = 28.7÷25, or 1.148 c.c. of the HCl. Hence the 950 c.c. of the KOH that remain must be diluted to 950×1.148, or 1090 c.c. to make them the equivalent of the N/2 HCl and therefore an N/2 KOH solution. This dilution is made as in the others with the alcohol that has been distilled in the presence of KOH.

Calculations.—In actual work the N/2 KOH does not remain for any length of time exactly of N/2 strength so it is more convenient to determine its exact relation to the N/2 HCl, which latter acid should remain unchanged. Suppose it is found as a result of the mean of several titrations of the HCl against the KHO that the 29.2 c.c. N/2 HCl equal 30 c.c. of the KOH. Since 1 c.c. of N/2 HCl reacts with exactly 28.05 mgs. of KOH, 1 c.c. of the KOH solution being tested is equivalent to 28.05×29.2÷30 c.c., or 27.30 mgs. of KOH, which value can then be used at that time, instead of the factor 28.05 which can be used only when the KOH is exactly normal.

Flash and Fire Tests.—The author uses the open fire tester of **Tagliabue.**

Place a bed of chip graphite in the bottom of the tester. Fill the reservoir with the oil to within one-quarter inch of the top and raise the temperature at the rate of 15° per minute; try for a small flash of flame across the surface of the oil every 7°. After getting the flash make note of the temperature and continue to raise the same until the oil takes fire and note this temperature which is the fire test. For an igniter use a small glass jet in a rubber hose connection so that the flame coming from the jet is not more than one-eighth of an inch long. In using this small igniting flame draw it across the diameter of the surface of the oil and keep the little flame on a level with the top of the tester, making sure that the jet does not touch the oil at any time. Keep the tester surrounded with a sheet iron cylinder during the testing to protect it from draughts. This test should be always carried out under exactly the same conditions or the results will be discordant. When the burning test has been completed smother the flame at once with the cover that goes with the instrument, as this serves to put out the flame and makes the tester easier to clean for the next sample.

Consult Technical Paper No. 49, Dept. of Interior, Bureau of Mines, by Allen and Crossfield, 1913, on the Flash Point of Oils.

Cold Test.—Fill a 4-ounce, wide neck, glass-stoppered bottle about half full of the oil and place it in a freezing mixture consisting of 2 parts of ice and 1 part of salt, which can be kept in a small can wrapped with asbestos. After the oil is solid, let it stand in the mixture for about an hour. Then take out the bottle and place a thermometer in it and stir with the thermometer until the oil will just flow from one end of the bottle to the other. The cold test is that temperature at which the oil will just flow.

Test for Free Acid.—This test is usually reported in grams of free oleic acid and N/6 KOH is used for the purpose, 1 c.c. of which is equal to 0.047 gram of free oleic acid. Weigh 8 to 10 grams of the oil, accurately, into a 250 c.c. cone flask. Add 100 c.c. of the redistilled alcohol prepared as given under Saponification. Put the flask in a water bath and bring the contents quickly to just 60° C. Then take the flask off the bath at once and titrate with the N/6 KOH until the first pink color just spreads through the test. Do not carry the titration any further or the result will be too high due to a certain amount of saponification taking place. The number of c.c. required to produce this first pink, multiplied by 0.047 and divided by the weight taken gives the amount of free oleic acid per gram which is then reported in percentage.

The alcohol used in these tests can be recovered by distilling off the same after the tests are completed. Add some quicklime to the fluid before distilling off the alcohol to remove any water.

Viscosity.—Any of the viscosimeters on the market can be used for this test. The author also uses the Tagliabue instrument for this work. Full directions go with these instruments so that but a brief hint or two is all that is necessary. For testing the oil at 70° attach the nipple marked 70° to the outlet and be sure that the oil has no dirt in it. If the room temperature is above 70° pour 90 c.c. of the oil into the container and just as soon as the oil reaches the required temperature allow 70 c.c. to pass through the nipple, timing its flow in seconds with a stop watch. The number of seconds required multiplied by two gives the viscosity.

To test oil at 212° water is brought to that temperature in the boiler of the viscosimeter, and the steam coming from the water passes through the steam jacket of the instrument which surrounds the oil container. Eighty c.c. of the sample which has already been heated to 22° or more are now placed in the oil container, and when the 212° are reached in the oil, as shown by the thermometer that goes with the instrument, 60 c.c. of the oil are withdrawn through the nipple marked 212° and the time of its flow is recorded in seconds with the stop watch. The seconds required multiplied by two give the viscosity.

The Engler viscosimeter refers all viscosity values to the same figures obtained by passing distilled water through his instrument. The figures obtained on the oil tested are divided by those gotten from water in the same way. This gives what he terms the specific viscosity.

The viscosimeter should be cleaned with ether after each test to prevent any gummy coating forming on the walls of the nipples, which would impair the accuracy of the instrument. The viscosity of water for this instrument used in this laboratory was found to be 40 at 70° and 75 at 212°.

Specific Gravity.—For the determination of specific gravity the Eichhorn picnometer is used. Cool the oil to 60° F. and fill the little bulb slowly with the oil so that no air bubbles enter with the oil, as the presence of air in the reservoir renders the result entirely inaccurate. Hold the picnometer at about a 70° angle when filling it so that the bubbles may be worked out to a better advantage. When the bulb is entirely full of the oil, and free of air, stopper it, wipe it free of oil, place it in a cylinder of water which is at 60° F. and read the specific gravity from the graduation of the instrument that is tangent to the meniscus curve of the surface of the water.

Some Specifications for Oils

Engine oils.

1. Flashing-point above 400° F.
2. It must be a pure mineral hydrocarbon oil, free from adulteration.
3. Its specific gravity must be between 26° and 30° Baumé.
4. Its viscosity (compared with water at 60° F., using a P.R.R. standard 100 c.c. pipette) must be, when determined at 80° F., not less than 2.5.
5. The oil must be free from acids, sulphur compounds or any other corrosive substances, and free from dirt or any other gritty material.

Heavy Dark Engine Oil.

1. Flashing-point above 450° F.
2. Its viscosity (compared with water at 60° F., using a P.R.R. standard 100 c.c. pipette), when determined at 80° F., must not be less than 2.5.
3. The oil must be free from all sulphur compounds, acid or any other corrosive substances of any kind, and free from dirt or any gritty substances.
4. Its specific gravity must be between 26° and 30° Baumé.

Cylinder Oil.

1. It must have a flashing-point of not less than 550° F.
2. Its specific gravity must be between 25° and 26° Baumé.
3. Its viscosity (compared with water at 60° F., using a P.R.R. standard 100 c.c. pipette), when determined at 330° F., must not be less than 1.25.
4. It must contain no saponifiable animal oil, and be a pure mineral hydrocarbon oil, free from adulterations.

5. The oil must be free from sulphur compounds, acids or any other corrosive substances of any kind, and must be free from dirt or any gritty substances.

Journal and Roll Neck Grease.

1. It must be free from all dirt and grit of any kind, acid or corrosive substances.
2. It must be absolutely neutral in reaction and free from metallic oxides, other than lime.

Torch Oil.

1. It must have a flashing-point of not less than 125° F.
2. It must show a fire test not below 150° F.
3. Its specific gravity must be between 44° and 48° Baumé at 60° F.
4. It must not become cloudy when cooled at 0° F.
5. This oil must be pure petroleum oil, free from dirt, grit, lumps, water, etc.

Paraffine Oil.

1. This oil must be neutral in reaction, free from all dirt or similar substances, and may have a flashing-point as low as 200° F. It must be pure petroleum oil.
2. Its viscosity (compared with water at 60° F., using a P.R.R. standard 100 c.c. pipette), when determined at 60° F., should not be less than 1.2.

Screw Cutting Oil.

1. This oil shall consist of paraffine oil of about 27° Baumé gravity compounded with not less than 25 per cent by weight of fat oil, cotton seed preferred.
2. The compounded oil shall have a flashing-point not below 300° F. and a burning point not above 425° F.

Fish Oil.

1. It must have a flashing-point of not lower than 525° F.
2. It must congeal at 43° F.
3. It must be free from soaps of any kind.
4. It must have a specific gravity of 21° Baumé.
5. It must be free from dirt and impurities.

Barrels must be in good condition, and should any barrel contain water, dirt, or other impurities it will be rejected.

NOTE.—The foregoing specifications follow very closely those gotten out by the Philadelphia & Reading R. R. under Robt. Job.

Viscosity by the Universal Standard Saybolt Viscosimeter.—The following viscosity figures were recently recommended to the author by a chemist of much experience in the manufacture of lubricants:

Engine oil at 100° F., 150 to 200 viscosity; average 160 to 180.

Heavy, dark engine oil at 130° F., 175 to 250 viscosity; average 200.

Cylinder oil at 212° F., 150 to 200 viscosity; average 160 to 170.

Paraffine oil at 100° F., 110 to 150; for light work, 100, and for heavy work, 150 viscosity. The Saybolt viscosimeter is widely used.

RESULTS OF SOME OIL TESTS

Cylinder Oil

	Acid Test.	Flash	Fire	Viscosity, 212° F	Sp. Grav.	Sap Val.	Cold Test
2/7/12.	Per Cent	Degrees	Degrees				Degrees
United....	0 168	546	628	153	0 895	20 53	40
Cylinder oil....	0 279	555	630	184	0.89	22 61	37
Capitol.......	0 232	566	646	197	0 898	22 24	36
Dark crescent....	..	. .	. .	.	. . .	....	....
3/18/12							
Capitol	0.126	505	558	161	0 914	18 30	39
8/13/12.							
Special 600........	0 00496	492	526	139	0 910	22 45	26
High standard.. ..	0 00215	508	552	185	0 918	17 84	30
No. 1 Oil City Oil ..	0.0010	590	642	189	0 890	16 93	37
No. 2 Oil City Oil ..	0.00108	555	622	162	0 884	16.45	32
....	0 00223	505	570	148	0 880	21 25	42
....	0.003	462	522	125	0 882	8 98	44
Capitol cylinder oil .	0 002	551	618	178	0 893	6 41	41

Lubricating Oil

	Acid Test	Flash	Fire	Viscosity, 212° F	Sp Grav.	Sap Val.	Cold Test
Brook's	0 144	558	628	160	0 892	17.60	35
Young's	0 113	530	588	134	0 895	30 24	46
Voegley	0 258	546	624	185	0 896	21.78	40
W. V. Lub....... .. .	0 139	357	399	102	0 884	8.029	15

Miscellaneous Oils

	Acid Test	Flash	Fire	Viscosity, 212° F	Sp Grav 60° F	Cold Test.	Sap Val.
8/22/12.							
Roll oil.............	0 016	404	459	187	0 870	17°F.	20.12
Tempering oil.........	0 0038	488	552	142	0 860	35.6°F.	2.82
Torch oil......... ...	. . .	205	229	50	0.844	....	5.5

	Sap. Value.	Viscosity at 70° F.	Viscosity at 212° F	Flash Point.	Fire Test.
3/27/11.					
Mineral lard oil cutting oil............	61	183	92	384	452

CHAPTER XIX

PART II

THE TESTING OF COAL

External Moisture.—By this term is meant the rain, snow, or mine, or barge water adhering to the surfaces of the coal. For this determination samples should be put at once into Mason jars supplied with screw tops and rubber washers or gaskets. The jars should be filled at the place of sampling and the tops screwed down, tightly, on the rubber. The jars can then be taken to the laboratory and allowed to attain the room temperature and weighed without opening them. After getting this weight, the jars are opened and the contents are spread out in thin layers, taking care that this operation is performed without the smallest loss of the weighed coal. The opened jars are placed in a bath of hot air to dry. The rubbers are removed and marked the same as their respective jars during the drying of the latter at a temperature of about 80° C. The contents of the jars are also labeled and are dried, without any crushing, at a temperature of 100° C. for several hours until all evidences of external dampness is gone and the fines in the samples have a tendency to be dusty. The tests are then returned to their respective containers; the rubbers and tops are also returned to their jars. The jars and their dried contents are again weighed after regaining the room temperature. The dry, empty jars with caps and rubbers on were also weighed in the meantime. The weight of the jars and the wet contents less the weight of the jars and the dry contents equals the weight of external moisture. The weight of the external moisture multiplied by 100 and divided by the weight of the corresponding jar and wet contents, from which has been deducted the weight of the dry empty jar, constitutes the per cent of external moisture. All weights referred to are taken with the caps and rubbers on the jars and are made on a torsion balance. This balance is of 10 kilos capacity and sensitive to a tenth of a gram. For these tests large samples are taken, from 1 to 2 pounds.

Internal Moisture.—The sample after being used for the determination of the external moisture is crushed to 100 mesh or finer and 1 gram of the powdered coal is dried for one hour at 105° C. The loss of weight constitutes the internal moisture which is reported in percentage. The sample is dried in a 20 c.c. platinum crucible.

Volatile Matter.—Place the crucible containing the sample on which the internal moisture determination was made in a ni-chrome triangle supported 8 cm. above the top of a Bunsen burner and play a flame 10 cm. high back and forth across the bottom of the crucible which is covered with a tightly fitting lid. Continue this heating for four minutes. Then place the burner directly under the crucible with the flame stationary and increase the length of the flame to 20 cm. Continue to heat for seven minutes more. Cool in a desiccator and weigh. The loss of weight constitutes the volatile matter.

The Committee on Coal Analysis of the American Society for Testing Materials and the American Chemical Society recommend that the volatile matter be determined in a 10 gram platinum crucible, using a capsule lid, that is, one that fits inside the crucible. The crucible and its 1 gram sample can then be placed in a muffle heated to 950° C. and maintained at this temperature for seven minutes. The author would prefer to use an electrically heated muffle furnace * which every laboratory should have, without fail, and can make at a low cost for this purpose. See Making and Repairing of Laboratory Electric Furnaces, page 505. The crucible is placed on a ni-chrome triangle support bent so as to keep the bottom of the crucible clear of the floor of the furnace.

Fixed Carbon and Ash.—The residue remaining in the crucible after the determination of the volatile matter is heated to a dull red and maintained at this heat until all carbon is burned away. The operation can be facilitated by supporting the crucible in a slanting position with the lid only partly covering it. Also occasional stirring of the mass in the crucible, using great care to prevent loss of the ash, will expedite the removal of the carbon. When the ash has assumed a uniform gray or reddish color free of all black material, the crucible is transferred to a desiccator, cooled and weighed. The loss of weight due to this removal of carbon is calculated to percentage as fixed carbon, on a basis of 1 gram.

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* The electric muffle is ventilated by a regulated stream of air drawn from the compressed-air pipe.

The ash found in the fixed carbon determination can be calculated as such to percentage or the ash can be gotten on a separate 1 gram sample. The freshly weighed sample is at first smoked off on a Bunsen burner as described in the determination of the volatile matter. The crucible is then raised to a dull red heat after all smoking is over and the heating is continued as already described. The extensive preliminary report of the committee above mentioned can be found in the Journal of Industrial and Engineering Chemistry, Vol. 5, No. 6, pages 517–528.

Heat Units.—Any of the well-known calorimeters can be used for this work. As the details of the operations of the instruments are always furnished with the latter, it seems quite unnecessary to repeat them here. The author would recommend that operator check his work and the instrument against some convenient material of known heat units. For this work the author has a standard coal powder on which the heat units were determined by the U. S. Bureau of Standards and a sample of the standard benzoic acid which is also furnished by the same institution for a small fee. The checking should be done at frequent intervals during the operation of the calorimeter.

Sulphur.—Grind together in an agate mortar 4 grams of magnesia and 2 grams of sodium carbonate until an intimate mixture of these materials is obtained. Mix thoroughly with four-fifths of this mixture 1 gram of the finely powdered coal in a platinum or porcelain crucible. Then put the other one-fifth of the mixture as a layer on top of the mixture of coal powder, magnesia and sodium carbonate. Place the crucible in an inclined position over the low flame of a Bunsen burner. Move the flame slowly back and forth under the crucible until it is very gradually brought to a low red heat on the bottom, and the mixture glows faintly under the top layer, as can be ascertained by giving the mass a slight stir with a ni-chrome wire. Continue this low heating until all black due to carbon is gone. Stir the mass at intervals.

Transfer the residue in the crucible, when the carbon is gone, to a casserole. Rinse out the crucible with about 40 c.c. of water, adding the rinsings to the residue in the casserole. Add 70 c.c. of bromine water to the casserole, cover it with a watch glass, boil ten minutes, remove the cover, add 50 c.c. of conc. HCl and evaporate to dryness. Cool, add 20 c.c. of conc. HCl, heat, add 100 c.c. of water, filter out any insoluble matter and wash with dilute HCl. Dilute the filtrate and washings to 300 c.c. Heat to boiling and add 25 c.c. of a saturated solution of barium chloride diluted with 75 c.c. of water. Let the barium sulphate settle for several hours, preferably overnight. Finish as in gravimetric sulphur in steels.

For a check the operator can carry through the factor weight as recommended by the before mentioned committee. The above is a modified form of the Eschka method. Blanks should be carried through all of the above operations and deducted.

For a check method 1 gram of the powdered coal can be fused in the calorimeter bomb with sodium peroxide and potassium chlorate per directions given with the calorimeter. Also 0.5 gram of coal can be fused in a platinum crucible with a mixture of 15 grams of sodium carbonate and 5 grams of potassium nitrate, dissolved out in water, transferred to a casserole, acidulated with HCl and finished as in the Eschka method. A further check method is to fuse 0.5 gram of the powdered coal with a mixture of 15 grams of sodium peroxide and 7.5 grams of sodium carbonate in an iron crucible. The melt is dissolved out in water, acidulated with HCl and finished as in the other methods.

The barium sulphate, obtained by any of the methods given, must be moistened with a few drops of dilute sulphuric acid after it has been ignited free of carbon. It is then ignited again to free it of the excess of the sulphuric acid. This insures against the presence of barium sulphite due to the reducing action of the burning filter paper.

Phosphorus.—Obtain the ash from 1.63 grams of the coal by burning the same on a low flame in a 20 gram platinum crucible. Fuse the ash with twenty times its weight of sodium carbonate and 0.100 gram of niter. Dissolve out the fusion with water, and transfer it to a casserole and acidulate with HCl, keeping the casserole covered to avoid loss. Heat until all spraying is over; evaporate to dryness, cool, redissolve by first heating with 10 c.c. of conc. HCl. Add 50 c.c. of water. Heat, filter, add a few drops of ferric chloride solution unless there is enough iron present to give a red precipitate with ammonia in the filtrate and washings. Wash the ammonia precipitate a few times with water and then dissolve it off the filter with 20 c.c. of 1.20 nitric acid. Use the acid hot and pour it back on the filter until all of the iron hydroxide, which will carry all of the phosphorus, is dissolved off the filter. Wash the filter with some 1 : 40 nitric acid about twenty times or until the washings do not give an appreciable iron test with KCNS. Evaporate the filtrate and washings to 15 c.c. Add 15 c.c. of water, boil with a slight excess of $KMnO_4$ solution, clear the excess of manganese oxide away with ferrous sulphate, add molybdate to the hot solution and finish as in steel.

Those who are interested in more elaborate details are referred to the preliminary report of the committee already referred to, or to Technical Paper No. 8 of the Department of the Interior, Bureau of Mines, Washington, D. C., Entitled Methods of Analyzing Coal and Coke, by Frederick M. Stanton and Arne C. Fieldner. The authors also give the method they use for the determination of nitrogen in coal. The preliminary report of the Committee on Coal Analysis can be found in Vol. 5, No. 6, of the Journal of Industrial and Eng. Chemistry.

Coke Analysis.—*Carbon.*—The author determines the total carbon, as in the analysis of graphite, by burning 0.200 gram of the coke in the electric combustion furnace.

The sulphur is obtained by fusing 0.5 gram of the coke in an iron crucible with 15 grams of sodium peroxide mixed with 10 grams of sodium carbonate. The fusion is then dissolved out with water and finished as given for sulphur in coal.

The ash is obtained as in coal.

THE DETERMINATION OF SULPHUR IN CRUDE PETROLEUM

Method No. 1.—The steel chemist is occasionally called upon to report on the sulphur content of crude oil. The following methods check nicely: Make an intimate mixture of 15 grams of dry sodium peroxide and 7½ grams of sodium carbonate. Place about two-thirds of this mixture in an iron crucible. Stir into it 0.2 gram of the oil. Do not use over 0.3 gram of the oil or it will explode when the heat is applied. Then put on the top of the oil and the $Na_2O_2+Na_2CO_3$ mixture, the balance of the Na_2O_2 and sodium carbonate. Then apply heat gently until the reaction is over. Then heat until the flux is melted; dissolve out the fusion; acidulate it with HCl; evaporate; take up in HCl and water; filter and precipitate the sulphuric acid formed with barium chloride, and finish the sulphur in the usual way.

Method No. 2.—Place 1 gram of potassium chlorate, 0.2 gram of benzoic acid, and 15 grams of sodium peroxide in the cartridge of a Parr or other calorimeter. Stir into this 0.2 gram of the oil until the mixture is complete. Then fire the mixture as in a heat unit determination. This method is given by Parr. Finish as in Method No. 1.

An oil that gave very high sulphur steel when it was used as fuel in the open hearth furnace showed the following sulphur by the two methods:

	No 1 Method	No 2 Method.
	Per Cent	Per Cent
Sulphur	3 89	3 70 3 71

CHAPTER XX

PART I

THE PERCENTAGE REDUCTION OF A SUBSTANCE IN SOLUTION TO ANY DESIRED PERCENTAGE

LET P = the percentage of the substance in the concentrated solution;
p = the lower and desired percentage of the substance;
A = the specific gravity of the concentrated solution;
W = the amount of water necessary to add to 1 c.c. of the conc. solution to reduce it to the desired lower percentage.

Then
$$W=\left(\frac{P-p}{p}\right)A.$$

Calculations.—Suppose the specific gravity of a given sample of nitric acid is found by means of a hydrometer to be 1.400 at a temperature of 20° C. By table No. 1 we find that the difference in specific gravity for 1° C. between 1.37 sp. gr. and 1.405 is from 0.0013 to 0.0014, or a total difference of 0.0001 for a variation of 0.035 in specific gravity. Now 1.400 is 0.030 above 1.37 in specific gravity, therefore the correction for 1° at 1.400 is $0.0013+\frac{30}{35}$ of 0.0001, or $0.0013+0.000085$, or 0.001385. Since the temperature was 20°, then the specific gravity of the given acid if cooled to 15° would be $1.40+0.00138\times 5$, or 1.4069. By the table we find that the nearest specific gravity, or 1.405, gives a percentage of 66.40. Further, the percentage correction at this point for 0.001 of specific gravity is 0.220. Therefore, the percentage of the given concentrated acid at 15° would be $66.40+0.220\times 1.9$, or $66.4+0.418$, or 66.818, or P in the reduction formula.

For example, if it is desired to reduce this 66.818 per cent acid at 15° to 32 per cent acid at 15°, then we have $\frac{66.818-32.00}{32.00}\times$.

1.4069, or $\frac{34.818}{32}\times 1.4069$, or 1.088×1.4069, or 1.530, or every c.c. of the acid requires 1.5307 c.c. of water to reduce it to 32 per cent at 15° C. By consulting table No. 2 it will be seen that 1000 c.c. acid of 1.407 specific gravity requires 1531.8 c.c. of water to reduce it to 32 per cent acid at 15° C.

In like manner, if it is required to obtain 20 per cent acid from 66.818 per cent acid: $\frac{66.818-20}{20}\times 1.4069$, or $\frac{46.818}{20}\times 1.4069$, or 2.3409×1.4069, or 3.2934. That is, 1 c.c. of 66.818 per cent acid requires 3.2934 c.c. of water to dilute it to 20 per cent acid at 15° C.

Use of Table No. 2.—Having by means of Table No. 1 calculated the observed specific gravity to 15°, then from Table No. 2 the amount of water required to reduce such an acid to 32 per cent or 20 per cent is read either direct or by interpolation.

In a similar way one can reduce concentrated ammonia to any desired lower percentage, the only difference being that in calculating to 15° C. the correction for percentage is subtractive instead of additive as in the case of acids, the reason, of course, being that the greater the density of ammonia solution in water, the lower the percentage of NH_3 therein.

If one needs to prepare from concentrated ammonia an 11.50 per cent solution, first, dilute 2 parts of the former with 1 part of water and cool to the room temperature. Let the reading be 0.9385 at 23° C. The correction for 1° C. at 0.938 by Table No. 3 is 0.0004 for specific gravity. The total correction for the 8° is 0.0004×8, or 0.0032. The specific gravity of the ammonia at 15° is therefore $0.9385+0.0032$, or 0.9417. By the table the nearest lower specific gravity is 0.940, which corresponds to 15.63 per cent ammonia. The percentage correction for 0.001 of specific gravity at this point is 0.295. Therefore, the total correction is 0.295×1.7, or 0.5015. Hence, the percentage for a specific gravity of 0.9417 is $15.63-0.5015$, or 15.1285. To reduce this percentage to 11.50 the formula gives the following:

$$\frac{15.128-11.50}{11.50}\times 0.9417=0.297,$$

or 1 liter of this ammonia would require 297 c.c. of water to dilute it to 11.50 per cent at 15° C.

TABLE I.—AQUEOUS SOLUTIONS OF NITRIC ACID

From a Table by Lunge and Rey. Specific Gravities and Percentages HNO_3.

Specific Gravity, $d\frac{15°}{4°}$ C.	Percentage HNO_3.	Difference in Specific Gravity for 1° C. between 13° and 17°.	Difference in Percentage for 0.001 Specific Gravity.	Specific Gravity $d\frac{15°}{4°}$ C.	Percentage HNO_3.	Difference in Specific Gravity for 1° C between 13° and 17°.	Difference in Percentage for 0.001 Specific Gravity.
1.055	9.84	0.0003	.....	1.280	44.41	0.0009	0.154
1.060	10.68	0.0003	0.168	1.285	45.18	0.0010	0.154
1.065	11.51	0.0003	0.166	1.290	45.95	0.0010	0.154
1.070	12.33	0.0003	0.164	1.295	46.72	0.0010	0.154
1.075	13.15	0.0004	0.164	1.300	47.49	0.0010	0.154
1.080	13.95	0.0004	0.160	1.305	48.26	0.0010	0.154
1.085	14.74	0.0004	0.158	1.310	49.07	0.0010	0.162
1.090	15.53	0.0004	0.158	1.315	49.89	0.0011	0.164
1.095	16.32	0.0004	0.158	1.320	50.71	0.0011	0.164
1.100	17.11	0.0004	0.158	1.325	51.53	0.0011	0.164
1.105	17.89	0.0005	0.156	1.330	52.37	0.0011	0.168
1.110	18.67	0.0005	0.156	1.335	53.22	0.0011	0.170
1.115	19.45	0.0005	0.156	1.340	54.07	0.0011	0.170
1.120	20.23	0.0005	0.156	1.345	54.93	0.0011	0.172
1.125	21.00	0.0005	0.154	1.350	55.79	0.0011	0.172
1.130	21.77	0.0005	0.154	1.355	56.66	0.0012	0.174
1.135	22.54	0.0006	0.154	1.360	57.57	0.0012	0.182
1.140	23.31	0.0006	0.154	1.365	58.48	0.0012	0.182
1.145	24.08	0.0006	0.154	1.370	59.39	0.0013	0.182
1.150	24.84	0.0006	0.152	1.375	60.30	0.0013	0.182
1.155	25.60	0.0006	0.152	1.380	61.27	0.0013	0.194
1.160	26.36	0.0006	0.152	1.385	62.24	0.0013	0.194
1.165	27.12	0.0007	0.152	1.390	63.23	0.0013	0.198
1.170	27.88	0.0007	0.152	1.395	64.25	0.0013	0.204
1.175	28.63	0.0007	0.150	1.400	65.30	0.0013	0.210
1.180	29.38	0.0007	0.150	1.405	66.40	0.0014	0.220
1.185	30.13	0.0007	0.150	1.410	67.50	0.0014	0.220
1.190	30.88	0.0007	0.150	1.415	68.63	0.0014	0.226
1.195	31.62	0.0007	0.150	1.420	69.80	0.0014	0.234
1.200	32.36	0.0007	0.148	1.425	70.98	0.0014	0.236
1.205	33.09	0.0008	0.146	1.430	72.17	0.0014	0.238
1.210	33.82	0.0008	0.146	1.435	73.39	0.0014	0.244
1.215	34.55	0.0008	0.146	1.440	74.68	0.0015	0.258
1.220	35.28	0.0008	0.146	1.445	75.98	0.0015	0.260
1.225	36.03	0.0008	0.150	1.450	77.28	0.0015	0.260
1.230	36.78	0.0008	0.150	1.455	78.60	0.0015	0.264
1.235	37.53	0.0008	0.150	1.460	79.98	0.0015	0.276
1.240	38.29	0.0008	0.152	1.465	81.42	0.0015	0.288
1.245	39.05	0.0008	0.152	1.470	82.90	0.0015	0.296
1.250	39.82	0.0009	0.154	1.475	84.45	0.0015	0.310
1.255	40.58	0.0009	0.152	1.480	86.05	0.0015	0.320
1.260	41.34	0.0009	0.152	1.485	87.70	0.0015	0.330
1.265	42.10	0.0009	0.152	1.490	89.60	0.0015	0.420
1.270	42.87	0.0009	0.154	1.495	91.60	0.0016	0.400
1.275	43.64	0.0009	0.154	1.500	94.09	0.0016	0.498

TABLE II.—DILUTION OF CONCENTRATED NITRIC ACID

To 20 and 32 Per Cent

Specific Gravity HNO$_3$ at 15° C	Water Added to 1000 c c.		Variation in Weight, Water for 1° C	Specific Gravity HNO$_3$ at 15° C	Water Added to 1000 c c		Variation, in Weight, Water for 1° C.
	20 Per Cent	32 Per Cent			20 Per Cent	32 Per Cent	
1 395	3086 4	1405 9	1 38	1.433	3790 5	1831 7	1 88
1 396	3103 3	1415 8	1 39	1 434	3810 6	1843 9	1 90
1 397	3120 2	1425 7	1 40	1 435	3830 7	1856 1	1.91
1 398	3137 1	1435 7	1 41	1 436	3852 0	1869 0	1 92
1 399	3154 0	1445 6	1 42	1 437	3873 3	1881.9	1 94
1 400	3171 0	1456 9	1 43	1 438	3894 6	1894 8	1.96
1 401	3188 7	1467 1	1 44	1 439	3915 9	1907 7	1 98
1 402	3206 4	1477 4	1 46	1 440	3937 0	1920 6	2 00
1 403	3224 1	1487 6	1 47	1 441	3958 5	1933 7	2 02
1 404	3241 8	1497 9	1 48	1 442	3980 0	1946 8	2 03
1 405	3259 6	1510 4	1 49	1 443	4001 5	1959 9	2 05
1 406	3277 8	1521 1	1 50	1 444	4023 0	1973 0	2 06
1 407	3295 5	1531 8	1 52	1 445	4044 6	1986 0	2 07
1 408	3313 2	1542 5	1 53	1 446	4066 2	1999.2	2 09
1 409	3330 9	1553 2	1 55	1 447	4087 8	2012.4	2 10
1 410	3348 8	1564 2	1.57	1 448	4109 4	2025 6	2 11
1 411	3367 2	1575 3	1 58	1 449	4131 0	2038 8	2 12
1 412	3385 6	1586 4	1 59	1 450	4152 8	2051.8	2 13
1 413	3404 0	1597 5	1 60	1 451	4175 1	2065 2	2 15
1 414	3422 4	1608 6	1 61	1 452	4197 4	2078 6	2 17
1 415	3440.6	1619 7	1 62	1 453	4219 7	2092 0	2 19
1 416	3459 6	1631 2	1 63	1 454	4242 0	2105 4	2 21
1 417	3478 6	1642 7	1 65	1 455	4263 2	2118 8	2 22
1 418	3497 6	1654 2	1.66	1 456	4286 3	2132 9	2 24
1 419	3516 6	1665 7	1 68	1 457	4309 4	2147.0	2 25
1 420	3535 8	1677 4	1 70	1 458	4332 5	2161 1	2 26
1 421	3555 1	1689 1	1 70	1 459	4355 6	2175 2	2 27
1 422	3574 4	1700 8	1 70	1 460	4378 5	2189 1	2 28
1 423	3593 7	1712 5	1.70	1 461	4402 6	2203 7	2 30
1 424	3613 0	1724 2	1.70	1.462	4426 7	2218 3	2 32
1 425	3632 3	1735 8	1 72	1 463	4450 8	2232 9	2 34
1.426	3651 9	1747.6	1 72	1 464	4474 9	2247 5	2 36
1 427	3671 5	1759 4	1 74	1 465	4499 0	2262 3	2 38
1 428	3691 1	1771 2	1 77	1 466	4523 8	2277 5	2 41
1 429	3710 7	1783 0	1.79	1 467	4548 6	2292 7	2 44
1 430	3730 2	1795 1	1 82	1 468	4573 4	2307 9	2 47
1 431	3750 3	1807 3	1 84	1.469	4598 2	2323 1	2.50
1 432	3770 4	1819 5	1.85	1.470	4623.2	2338 3	2.55

For further illustration, suppose it is necessary to obtain the percentage of ammonia corresponding to a specific gravity of 0.947 at 22°. The correction for specific gravity per 1° of temperature at the nearest point in the table (0.946) is 0.00036. As the reading was taken 7° above the 15°, then the total correction is 0.00036×7, or 0.0C252, and the corrected reading is 0.947+0.00252, or 0.9495. The nearest lower specific gravity in

Table No. 3 is 0.948, being equivalent to a percentage of 13.31. Now the correction for percentage at this point is 0.285 for every 0.001 of specific gravity. The total correction is 0.285×1.5, or 0.427. The percentage of the ammonia for 0.9495 at 15° is 13.31−0.427, or 12.88 per cent.

TABLE III.—SPECIFIC GRAVITIES OF AMMONIA SOLUTIONS

Lunge and Wiernik.

Specific Gravity at 15° C	Per Cent NH_3	Difference in Specific Gravity for 1° C.	Difference in Per Cent for 0.001 Specific Gravity	Specific Gravity at 15° C	Per Cent NH_3	Difference in Specific Gravity for 1° C	Difference in Per Cent for 0.001 Specific Gravity
0.980	4.80	0.00023	. . .	0.930	18.64	0.00042	0.305
0.978	5.30	0.00023	0.250	0.928	19.25	0.00043	0.305
0.976	5.80	0.00024	0.250	0.926	19.87	0.00044	0.310
0.974	6.30	0.00024	0.250	0.924	20.49	0.00045	0.310
0.972	6.80	0.00025	0.250	0.922	21.12	0.00046	0.315
0.970	7.31	0.00025	0.255	0.920	21.75	0.00047	0.315
0.968	7.82	0.00026	0.255	0.918	22.39	0.00048	0.320
0.966	8.33	0.00026	0.255	0.916	23.03	0.00049	0.320
0.964	8.84	0.00027	0.255	0.914	23.68	0.00050	0.325
0.962	9.35	0.00028	0.255	0.912	24.33	0.00051	0.325
0.960	9.91	0.00029	0.280	0.910	24.99	0.00052	0.330
0.958	10.47	0.00030	0.280	0.908	25.65	0.00053	0.330
0.956	11.03	0.00031	0.280	0.906	26.31	0.00054	0.330
0.954	11.60	0.00032	0.285	0.904	26.98	0.00055	0.335
0.952	12.17	0.00033	0.285	0.902	27.65	0.00056	0.335
0.950	12.74	0.00034	0.285	0.900	28.33	0.00057	0.340
0.948	13.31	0.00035	0.285	0.898	29.01	0.00058	0.340
0.946	13.88	0.00036	0.285	0.896	29.69	0.00059	0.340
0.944	14.46	0.00037	0.290	0.894	30.37	0.00060	0.340
0.942	15.04	0.00038	0.290	0.892	31.05	0.00060	0.340
0.940	15.63	0.00039	0.295	0.890	31.75	0.00061	0.350
0.938	16.22	0.00040	0.295	0.888	32.50	0.00062	0.375
0.936	16.82	0.00041	0.300	0.886	33.25	0.00063	0.375
0.934	17.42	0.00041	0.300	0.884	34.10	0.00064	0.425
0.932	18.03	0.00042	0.305	0.882	34.95	0.00065	0.425

CHAPTER XX

PART II

PLAN AND VIEWS OF CHEMICAL LABORATORY FOR STEEL WORKS PRACTICE

THE working drawings show an extension planned by the author, and added to the laboratory of the Park Works of the Crucible Steel Co. of America. (Pages 484 and 490)

Central double tables are located at *D*, *D*, and single side tables at *H*, *F*, *E*, *J*, *I*, and a single center one at *G*, Fig. 39–1. Tables *D*, *D*, and *E* are supplied with gas at 8-ounce pressure, compressed air at about 80 pounds and water as shown. At the small deep stone sinks on the ends of the tables are brass water power pumps. Illustration 20, page 298, gives a view of one of these suction outfits where four chromium-vanadium tests can be filtered through porous alundum thimbles, connected to one pump by means of a glass manifold. The circles represent the large wash bottles that are placed on high pedestals.

View 40 shows these bottles above the tables. No. 41 shows the hoods. The halves of *D*, *D*, Fig. 39–1, facing the center aisle are used for combustion work. There is abundant room for eight outfits, four on each half. View 42 shows four combustion furnaces with trains. The other halves of *D*, *D*, are for general analytical work and serve the hoods *C* and *B*, Fig. 39–1.

All hoods are equipped with water and extra heavy lead waste pipes for condensers. View 43 shows one of these brass water cocks of which there are two in each division of the hoods. View 43 also shows the way in which the gas is distributed to the various burners from gas cocks concealed in the hood cupboards below. All working surfaces of the hoods and the tables are covered with stone slabs. All heating apparatus is placed on an upper slab set on wooden cross pieces leaving an air space of about 1½ inches. This removes danger of the stone slabs being

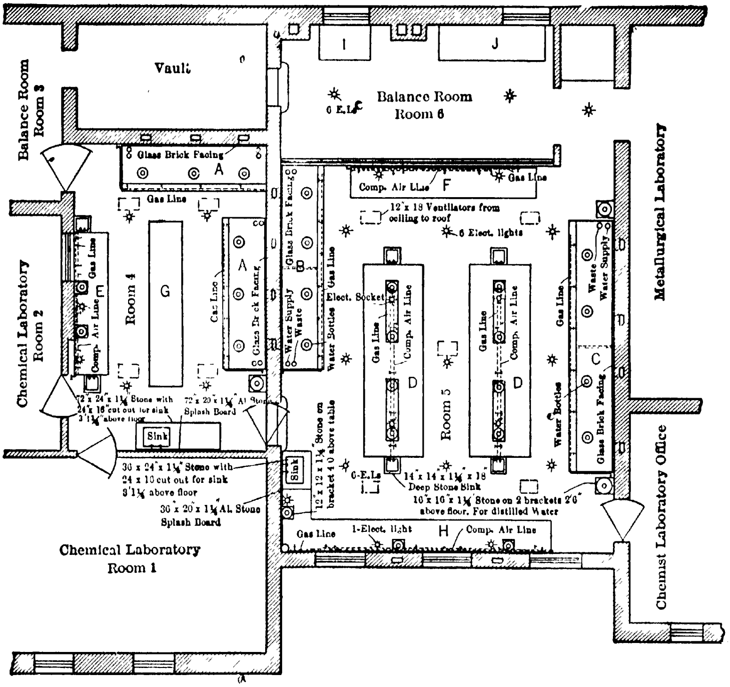
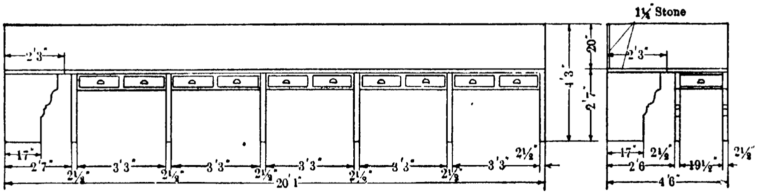
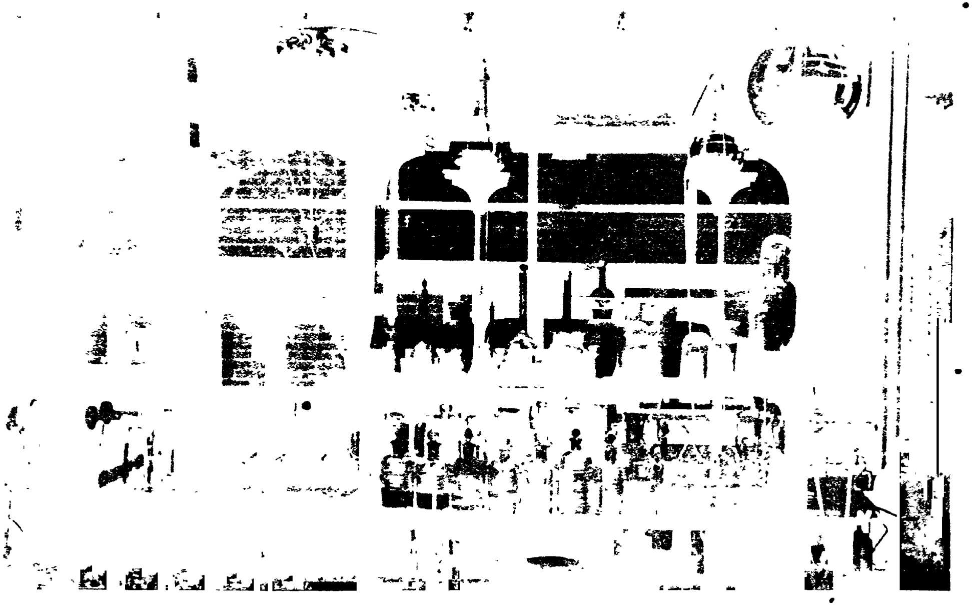

Vault
Balance Room
Room 6
Balance Room
Room 3
I
J
Glass Brick Facing
A
Gas Line
G
Room 4
E
Gas Line
Comp. Air Line
Chemical Laboratory
Room 2
72" x 24" x 1¼" Stone with 24" x 18" cut out for sink 3' 1¼" above floor
72" x 20" x 1¼" Al. Stone Splash Board
Sink
30 x 24" x 1¼" Stone with 24 x 10 cut out for sink 3' 1¼" above floor
30" x 20" x 1¼" Al. Stone Splash Board
Chemical Laboratory
Room 1
Glass Brick Facing
B
Water Supply
Waste
Water Bottles
Gas Line
12 x 12 x 1¼ Stone on bracket 4' 0" above table
Elect. Socket
Comp. Air Line
F
Gas Line
12" x 18 Ventilators from ceiling to roof
6 Elect. lights
6 E.L.
D
D
Room 5
6-E.Ls
14" x 14" x 1¼" x 18 Deep Stone Sink
10" x 16" x 1¼" Stone on 2 brackets 2' 0" above floor. For distilled Water
Gas Line
1-Elect. light
H
Comp. Air Line
Waste
Water Supply
C
Water Bottles
Glass Brick Facing
Metallurgical Laboratory
Chemist Laboratory Office

FIG. 39-1.

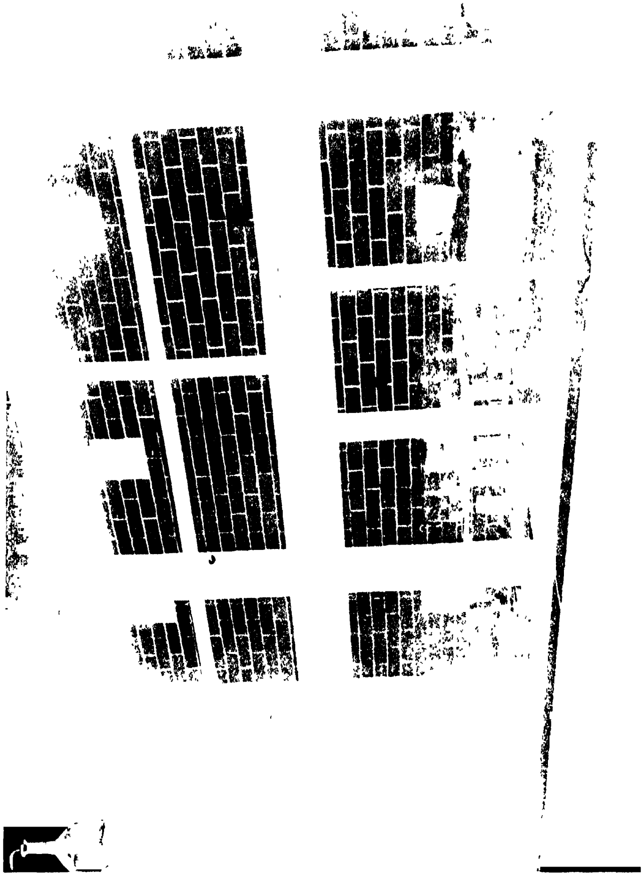


1-Table Req'd-H-1

FIG. 39-2.

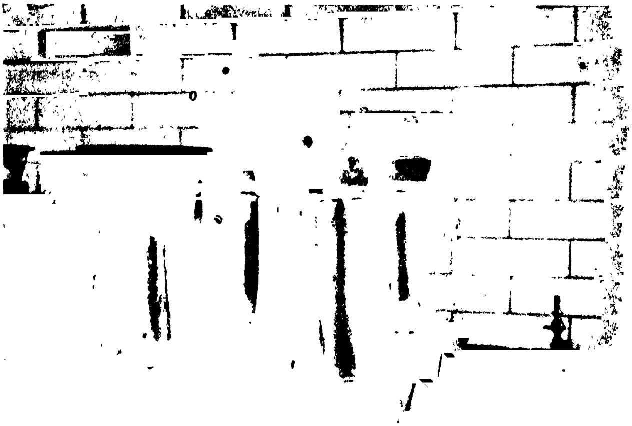


View 40.



VIEW 41.

View 42.



View 43.

View 44.

cracked by radiated heat. The back walls of hoods are of acid-proof brick with a white surface as shown in Views 41, 43, 44. The latter show the way the hoods are fitted with sliding doors and are framed with cabinet-finished straight-sawed oak. The sliding doors the author has found to be far superior to any others. The hoods along the walls of the laboratory are much to be preferred to center hoods. The latter cut off the light, do not have a good draught and cannot be backed with acid-proof material. Again the center hood is peculiarly subject to dirt dropping from its upper parts and its flues. If bits of mortar drop from flues, slanting sash can be set up as shown in the hood at the rear of View 44. These frames are supported on iron rods and can be removed in a few moments when it is desired to clean out the hoods. All tables, hoods, and exposed floor lines have stone baseboards to prevent the marring of the woodwork when the floors are mopped or scrubbed. The large sinks near the doorways are made of heavy acid-proof stoneware. The nipple at the outlet of the sink fits into a terra-cotta sewer via a trap of the same material. All joints are caulked with oakum and on top of the latter is poured hot

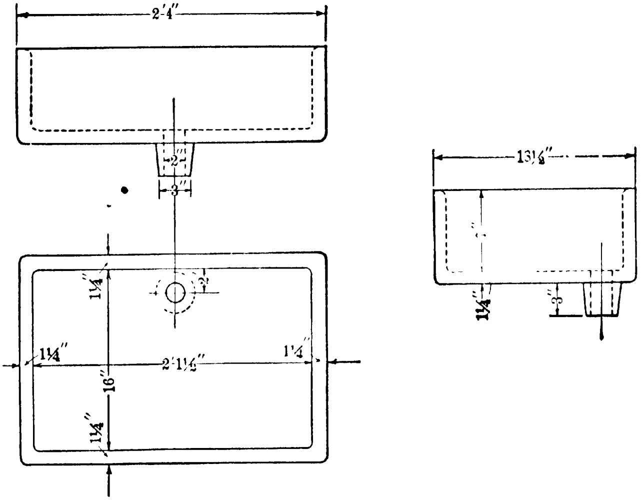
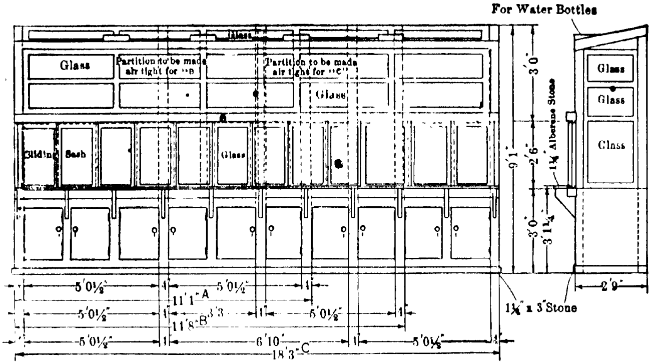
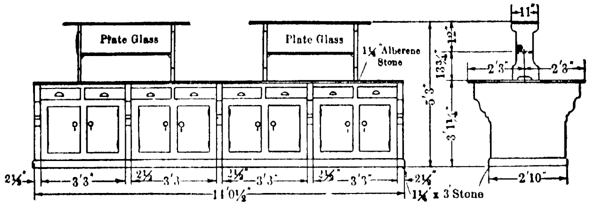


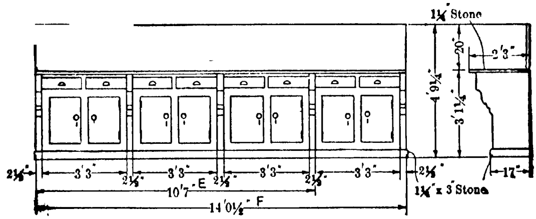
FIG. 45.



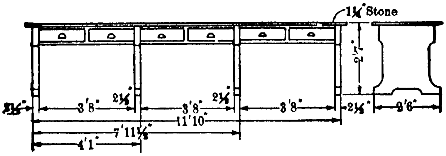
2-Hoods Req'd - A
1 " " - B -1
1 " " - C



2-Tables Req'd - D - 1



1-Table Req'd - E
1 " " - F -1



1-Table Req'd - G
1 " " - I
1 " " - J

FIG. 39-3.

asphaltum. The sinks of this description are practically indestructible. Fig. 45 gives the author's design and dimensions of this acid- and alkali-proof sink. The sewer from such a sink should never lead away from it in a horizontal direction. The terra-cotta sewer from any sink into which acid, alkali, or any corrosive waste is poured should drop vertically to the basement to prevent stoppages and leaks. To prevent broken glass and other odds and ends from getting from the sink into the sewer, a false bottom of oak, perforated with one-quarter inch holes, should be provided. To prevent the pitch from running out of the joints in hot weather, it is safer to finish off the joints with a final layer of cement plastered firmly on top of the pitch; it is absolutely necessary to do this when it is impossible to avoid placing a length or two of pipe horizontally.

The elevation of the balance table used in room 5 is shown in the drawing at *H*—1, Fig. 39-2, page 484. The elevations of the hoods and tables in rooms Nos. 4, 5, and 6 are given at *A*—1, *B*—1, *C*—1, *D*—1, *E*—1, *F*—1, *G*—1, *I*—1, and *J*—1, respectively (see Figs. 39-2-3).

The stone tops of all of the work tables are covered with sheet rubber packing of about one-eighth inch thickness. This material makes a nice appearance and prevents considerable breakage of glassware.

CHAPTER XX

PART III

MICROSCOPIC EXAMINATION OF STEEL

Preparation of Samples.—The author gives the following to save much time reading the long list of works on this subject published in the United States, England, and France for those of his readers who are novices in the microscopic examination of steel. The routine of the work is given in minute detail because success in this line of steel testing and study requires much painstaking attention for success. Imperfect polishing may put small depressions and irregularities in the specimen that render the microphotograph misleading.

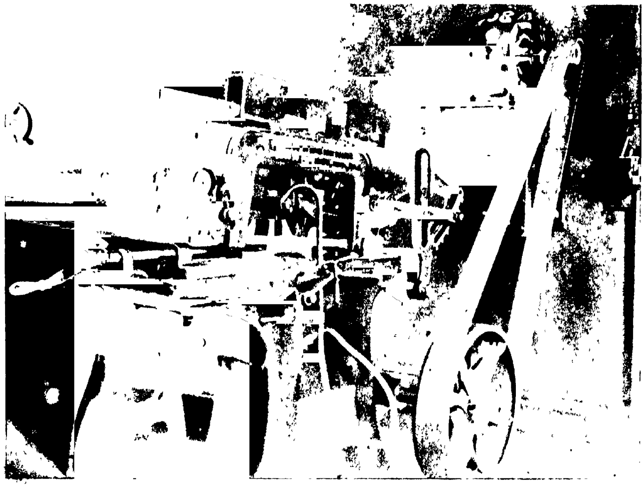


PHOTO 46.

For this work it is necessary to have several cutting-off machines. A power hack saw is required for cutting soft steel and annealed steel. The Starrett hack saw with 14-inch blade answers very well for cutting soft steel specimens or annealed steel (Photo 46).

For cutting hardened steel, Wilmarth Morgan No. 1.26 surface grinder equipped with alundum elastic cutting wheels

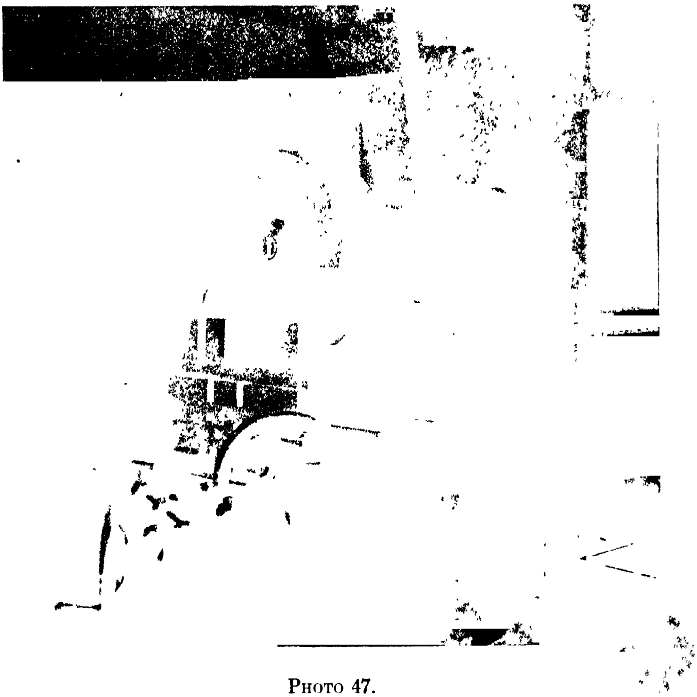


Photo 47.

12 inches diameter, $\frac{3}{32}$ inch thick by $1\frac{3}{8}$ inches, grit 24, grade G, running at 1500 r.p.m., will speedily cut through the hard high-speed steel. See Photo 47.

The section to be examined is cut from the piece submitted with power hack saw, if it is soft steel; grind off sharp edges and rough spots that are liable to hold fine particles of grit on a carborundum wheel. A convenient stone for this operation is an 8-inch diameter by 1 inch thick, grit 80, Grade G-5 (Carborundum Co.'s make). See Photo 48.

It is also necessary to have a two-wheel machine for this carborundum wheel. The surface to be polished is held against the side of this carborundum grindstone until the scratches of the previous cutting are removed. With every change of position during the cutting, the piece should be turned so that the new scratches will be at right angle to the previous ones. See Photo 48 for two-wheel machine.

Photo 48.

It is next held against a wheel covered with No. F Aloxit cloth (made by the Carborundum Co.) glued on a backing of a fiber board, screwed to a metal wheel disk on the two-wheel grinder. The scratches from the grindstone are held against the cloth until all scratches are gone. Also an endless belt polisher is very desirable at this stage. See Photo No. 49. It is next rubbed back and forth on No. 1 Hubert paper (French emery held by mucilage on plate glass). It is then further rubbed by hand on Nos. 0, 00, 000, French emery paper, if necessary. It is not always required to use all these grades of the Hubert paper.

As the cutting paper becomes finer the pressure on the piece should be lessened and care must be taken that no grit or dirt gets on the paper while rubbing the sample on it. After the final hand rubbing on No. 000 paper has been finished the piece is ready for the canvas wheel and carborundum mixture. The canvas wheel travels at 1275 r.p.m. See Photo No. 50.

Photo 49.

This wheel is made by stretching canvas over a brass disk and tying it to the wheel. The polishing medium is made as follows:

Carborundum (60 minutes)	300 gms.
Water	2400 c.c.
HNO_3 concentrated	20 c.c.

Mix in a large bottle (3000 c.c.) and allow to stand till the liquid is clear or very nearly so. By means of a siphon draw off the supernatant liquid and discard it. Fill the bottle with water again to the same mark and allow to stand. When clear or nearly so, siphon and discard the top liquid as before; and so on, until free of acid, or until supernatant liquid retains a milky appearance. This indicates the removal of all of the acid. Decant this cloudy liquid.

Fill the bottle again with water to the mark and shake thoroughly. Make the mixture very faintly ammoniacal. Shake it and let settle for ten minutes, siphon off the liquid to within about three-fourths inch from the bottom.

Photo 50

Keep this part just siphoned; shake it well and allow it to settle fifteen minutes. Siphon off the top liquid again, and keep the bottom mixture, which is the desired part.

For use dilute this bottom layer with about 10 parts of water. To use apply it to the center of the revolving canvas-covered wheel with a wash bottle. The sample is held lightly against the canvas. The canvas wheel has a copper guard which catches the excess polishing mixture and drains same away.

Buffing or Final Polishing.—A French felt, 10-inch jeweler's buffing wheel is used for this operation. Wheel travels at 1275 r.p.m. The felt wheel is also encased in copper guards to catch excess moisture and drain same off. The felt is coated with alumina-castile soap mixture made as follows:

Aluminum oxide	300 gms.
Water	2400 c.c.
KNO_3	20 c.c.

Mix in a 3-liter bottle and allow to settle till almost clear, taking about twenty-four hours. Siphon off the top liquid, fill again with water and repeat the operation after settling. Fill up again with water to 3 liters make very faintly ammoniacal. Shake thoroughly and set aside for fifteen minutes. Then siphon off and discard the sludge. Shake the siphoned fluid and set aside for thirty minutes. Siphon off the top liquid and keep the residue on the bottom which is of the desired fineness. This part is added to a solution made by dissolving 100 grams castile soap in 800 c.c. water, boiling the mixture of soap and alumina.

This mixture is applied to the felt wheel from a wash bottle. In polishing the piece it should be held very lightly against the wheel until all scratches are gone and the surface has a mirror-like appearance. The polished piece must be washed in running water and dried on a soft towel and is then ready for the microscope for examination and to be photographed for cracks and honeycombed structure (minute round cavities due to gas entrapped during the freezing of the metal). These are found in steel that has not been thoroughly killed before casting. Also slag enclosures and oval segregations of manganese sulphide are best shown in the unetched photograph.

On the microscope table a small wood block covered with the best grade of chamois skin should be at hand for rubbing dust particles or finger marks from the polished surface, immediately before microscopic examination.

The Etched Photograph.—The microstructure of the carbides, ferrite, pearlite, cementite, martensite, and austenite; and transition bodies such as sorbite and troostite are brought out by etching with various solutions. A good etching medium is 1 c.c. of conc. nitric acid mixed with 10 c.c. of absolute alcohol. Hardened steel is held in this solution from fifteen to thirty seconds. Then washed off in alcohol alone and blown dry at once with compressed air filtered through a large bottle filled with glass wool. Unhardened steel etches more rapidly and is held in the etching solution for from one second to thirty seconds, depending on the kind of steel.

Picric Etch.—Make a solution of picric acid in alcohol 10 grams dissolved in 100 c.c. of alcohol. To this add an equal volume of a solution of 2 c.c. of conc. nitric acid dissolved in 98 c.c. of alcohol.

Rosenhain's Reagent to Detect Phosphorus Segregation.—Dissolve 30 grams of ferric chloride, 100 c.c. of HCl, 1 gram of cupric chloride, and 0.5 gram of stannous chloride in 900 c.c. of water. For further details of etching solutions consult The Microscopic Analysis of Metals, by Osmond and Stead; Sauveur's Metallography of Iron and Steel, and the numerous other works on this subject.

Photographing of Samples.—*Focusing Specimens.*—The author uses the Leitz camera. See Photo No. 51. The specimens to be photographed should be placed on the table above the objective and the little arc light adjusted until the light is evenly distributed over the entire field. This is an important operation, as undesirable shading on the plate will occur unless each part of the field receives the same intensity of light. By means of the rack and pinion on the table bring the section to be photographed in the center of the field, after getting the correct focus. The field now is just as the finished photograph will appear.

Consult the chart showing the camera extension in centimeters, using the various eyepieces and objectives. For the ordinary work use eyepiece No. 2 and objective No. 3, the 100 diameter magnification requires the camera to be extended 68.5 cm. Pull out the eyepiece, which then allows the reflected light from the specimen to go through the camera and strike on the ground-glass plate in the back of the camera. Examine the figure closely to see that the picture is properly focused and the light evenly distributed. The light from the arc, if used directly, is entirely too strong, so a light filter must be used. Best results are obtained by using a green glass filter No. "B." Place the filter in the slot in the back end of the large condensing lens. Examine the image again on the ground-glass screen and then by means of the shutter on the condensing lens, cut off the light.

From the dark room get the plate holder containing the plate with the sensitive side of the plate next to the slide. Very carefully, so as not to disturb the position of the specimen, remove the ground-glass plate and insert the plate holder.

Exposure of Plate.—Pull out the slide on the plate holder, and with a stop watch at hand open the shutter on the con-

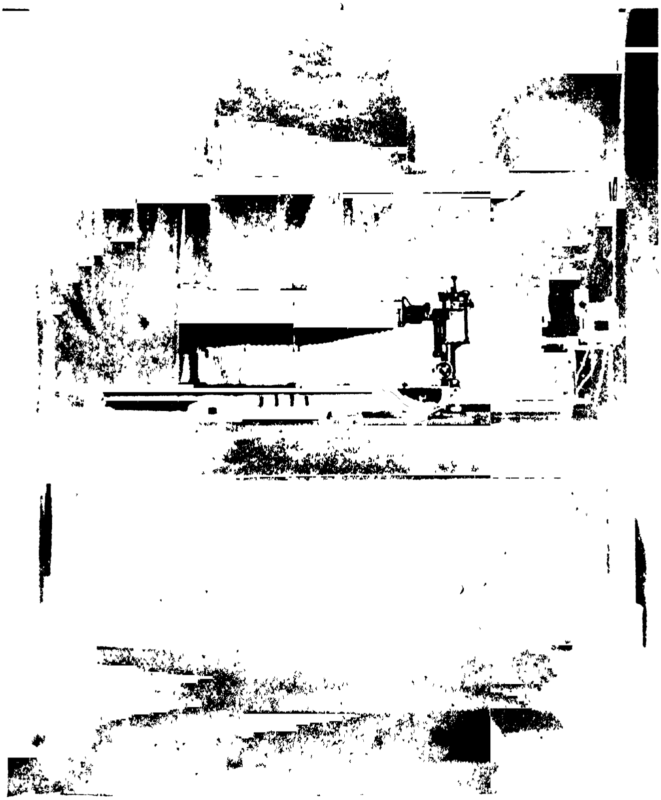


PHOTO 51.

densing lens, at the same instant starting the watch. The time allowed is a very important feature and must be estimated by several factors, namely, light intensity, nature of the piece being photographed, the kind and type of plate used, and the result to be produced. Unetched pieces require much less time for exposure than etched ones, as they reflect more light.

For our work we are at present using Wratten and Wainwright "M" plates, made by the Eastman Kodak Co. These plates require about ten seconds' exposure for unetched specimens and about twenty-five seconds for etched ones. During the time of the exposure do not jar the apparatus, as the picture may become blurred. When the exact time of exposure is reached, close the shutter and push back the slide on the plate holder. Remove the plate holder and replace the ground-glass plate and push in the eyepiece. The apparatus is then ready for the next specimen.

Developing.—Take plate holder to the dark room and remove the plate from the holder, the only light being that from the green safe light. The sensitive side of the plate is the white side; near one corner, on this side, mark the number of the picture with a pencil.

Immerse the plate in the developer with the sensitive side up and at the same time, start the stop-watch. The developer is made as follows, and should be poured into the mixture in the order as numbered below:

No. 1	1 4 grams of metal
No. 2	5 8 grams of hydroquinone
No. 3	21 0 grams of sodium sulphite
No. 4	39 0 grams of sodium carbonate

The above should be mixed in 900 c.c. distilled water.

In a large graduate measure 900 c.c. of distilled water. Use part of this water to dissolve each of the above in separate beakers. When the contents of each beaker are dissolved, pour all into a brown glass bottle and add the remainder of the water. A roll of strip zinc is kept in the bottle acting as a preservative for the developer. To use, pour enough developer in a hard rubber tray to cover the plate. Make up fresh as needed.

Using this developer, the time as stated before will require three minutes to develop the plate to the right point. When the time is up, remove the plate and hold by the edges under water, sensitive side down. With the fingers of the free hand rub off the black backing, being sure to remove it all. Turn the plate over; hold under the faucet and with the heel of the hand rub lightly the whole surface of the plate. Then place the plate in the tray containing the fixing bath made as follows:

Sodium thiosulphate	480 grams
Sodium sulphite	30 grams
Potassium aluminum sulphate	30 grams
A solution of glacial acetic acid, 28 c.c. and 72 c.c. water	

Dissolve the alum separately in 200 c.c. of water, the rest of the ingredients in 2000 c.c. of water. Then add the alum solution last, to prevent clouding.

After the developed and washed plate has been in this fixing solution for four minutes, light will not attack the plate, so it may now be examined by holding against an electric light. Keep it in the fixing bath for at least ten minutes, preferably fifteen. After this time is up place the plate in a tray of running water, film side up, and allow the water to wash it for a half hour or more. When washed, place in a plate drying rack till thoroughly dry. Care must be taken not to allow any dust to settle on the plates, and also during handling not to scratch the films. The proper temperature for all solutions is 60° to 65° F. When it is thought that the plate may have been over-exposed, add several drops of 10 per cent KBr in water to the developer. This retards the development.

Printing.—Place the plate in the printing frame with the film side up, then hold up to the light and adjust the mat over the part desired on the print. Hold the mat with the thumb and turn off the bright light, during printing a ruby lamp or orange shade should be used. Place a sheet of printing paper over the mat with the film side against the film side of the plate. Glossy velox paper is satisfactory. On the side of the paper which is now up, mark the same number which is on the plate. Put on the heavy blotter over the paper and then the back frame of the holder; snap the springs under the catches. Place the printing frame in the holder in the top of the light box (five lamps, 60 watts under ground-glass cover). The time of exposure depends on the intensity of the plate. The best method to get the correct time for exposure is to make several trial prints. The time of exposure varies from five seconds to 1½ minutes.

Ordinarily, plates of etched specimens require about ten to fifteen seconds' exposure. After the print is exposed remove the paper and place in a tray containing the same kind of developer used for the plates with several drops of KBr solution added. Immerse quickly and rock the tray slowly until the picture is at the desired intensity. Remove quickly and wash under the faucet for several seconds. Then place in a tray containing the same fixing bath used for the plates. It should remain in the fixing bath for twenty minutes. Light will not affect the print as soon as it is placed in the fixer. After the print is fixed for twenty minutes it should be washed in the same manner as for plates for at least one hour in bath of running water. Use a small tank with plate rack in it supporting the plates on edge in the rack. After washing, place picture side against the drying tin plate and with the rubber roller roll off as much water as possible. The print will drop off the drying plate when the drying is completed and picture is ready for mounting. The prints are cut on a trimming board (Eastman's).

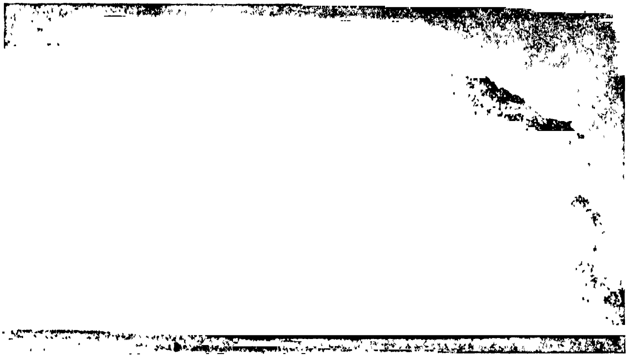


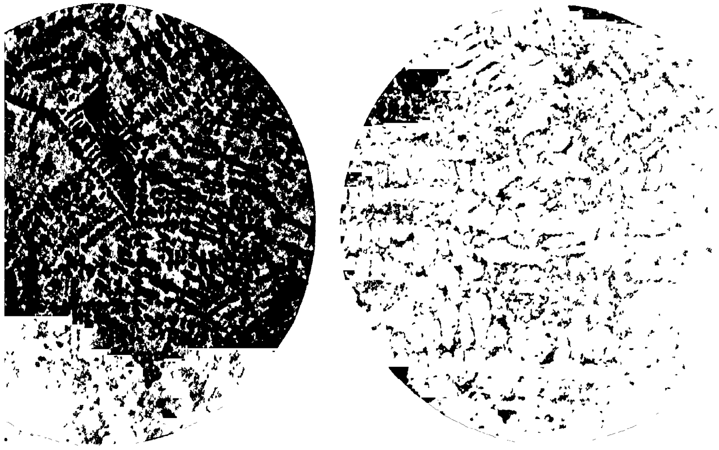
PHOTO 52.

Deep Etching with Dilute Sulphuric Acid.—In the second edition of "Special Steels," page 223, the author called attention to a scheme for detecting segregation; defects; and lack of soundness by etching polished steel surfaces with dilute H_2SO_4. The author now uses a mixture of 5 parts by volume of conc. sulphuric acid diluted with 20 parts of water. In this way, by allowing the acid to act for several hours, all sorts of defects can be detected that are never found by the microscope because of the exceedingly small portion of the area of the sample included in section taken for microscopic examination. By the etching method there is no limit as to size of the piece of steel that can be examined, except the dimensions of the etching tank. For such tests, except for the detection of exceedingly small flaws, a high polish is not necessary. Simply a comparatively smooth surface is needed. The pickling should be continued until all of the scale has been removed from the unpolished parts. Photo No. 52 shows a sample of steel containing many minute defects that the flow of the metal during high polishing may hide or the section being polished may not include. A long etch of several hours tells the story of why the steel failed.

ETCHING SOLUTION FOR 14% CHROMIUM STEEL AND STELLITE

Immerse for two minutes, if necessary, in the following: Dilute 5 c.c. of conc. HCl with 20 c.c. of iso-amyl-alcohol and add 8 to 9 c.c. of a saturated solution of picric acid in alcohol (grain alcohol). Fig. B shows the structure of stellite after being etched by the foregoing mixture which is substantially the same as recommended by Kourbatoff. (Revue de Met. mars., 1905, p. 186.)

FIG. B



Stellite ×200 Trans

Stellite ×300 Long

CHAPTER XX

PART IV

THE MAKING AND REPAIRING OF LABORATORY ELECTRIC FURNACES

IT is quite an economy and instructive for the chemist to build and repair his own electric muffle and combustion furnaces. The modern laboratory cannot afford to be without such equipment. The author used a true ni-chrome wire of German manufacture. For the carbon combustion furnaces, No. 20-gauge wire, 0.032 diameter, is a convenient size. Its resistance is 0.537 ohm per foot. With a voltage ranging as high as 240, direct current, 90 feet of this size is about right and gives a service of three or more months, running twenty-four hours per day. The wire is coiled around a three-sixteenth diameter rod held in guides and run by a one-half horse-power motor.

The expressage is saved to and from the professional repairman and the delay of waiting for the return of the apparatus is avoided.

The coiled wire is wrapped spirally around the clay core, taking precaution that the turns of the spiral do not touch each other as they wind around the core. The ends of the coil are secured at each end of the core with asbestos cord, being tied to the latter. The turns of the wire are then covered with a blanket of alundum or zirconia cement. The core is put in a warm place until dry. At each end of the coil 2 or 3 inches of the wire are left uncoiled for connection with the power. One of the cores with the wire on it is shown in Fig. 18, page 293. The cement is plastered over the spiral of wire, shown in the figure. The chemist can readily follow these details by taking such a furnace apart.†

The author ventilates his electric muffle furnaces when igniting filter papers, etc., by blowing a regulated stream of air through the furnace.

† The author is now trying the plan of wiring directly on his tapered clay

A large muffle furnace can be built by any laboratory. A sheet iron frame can be used for the sides. The top and bottom of the shell can be in the form of lids of the same material. It is well to place at the top and bottom of each corner of the frame, and on the inside of it, right angle strips of hoop iron. These make the shell more rigid. The opening for the muffle should be central and the frame or shell should be just as deep as the muffle is long, so that the muffle will rest in the frame and come just flush with the outside of the shell. The muffle opening in the frame should fit exactly around the outside of the ends of the muffle, so that very little plastering around it with the cement will be necessary. The author uses No. 17 gauge wire for the muffle furnaces, that is, 0.045 inch diameter. Three coils are wound around the muffle and connected in parallel. The writer places the parallel leads on the *outside* of the furnace shell, thereby keeping the leads away from the heat, and more accessible. The leads are enclosed in red fiber insulating tubes and supported in brass brackets. One lead is placed on the right side of the furnace shell and the other on the left side. This gives a neat appearance. Where the ends of the coils pass through the metal shell, they are carried through small quartz or pipe-clay insulating tubes to join the leads. Each coil is 120 feet long for a 240 volt, direct current. The heat is regulated by means of a rheostat (see Photo No. 3, page 119) of 14 to 25 amps. capacity. The doors are sheet iron, lined with fire-brick. They slide up and down* in sheet-iron guides and are hung on a lever. The leads are of No. 8 gauge ni-chrome wire of the same make as the heating wire. The furnace shell is given a coat of stovepipe enamel and, if preferred, it can be then given a white finish consisting of two coats of aluminum paint. Fifty pounds of magnesia oxide are needed to fill in all spaces around the core and retain the heat. The entire inside of the shell except the space occupied by the muffle is filled with this non-conducting powder. Four right-angle strips of sheet brass about one-eighth inch thick will be needed to support the

combustion tube. This gives a combustion furnace that will come to full heat in thirty minutes, and saves the cost of the core tube.

* Or the door can be made to open on side hinges, horizontally. Such a door can be lined with a fire-brick that fits the muffle opening and projects into the same. This liner keeps heat in better than one that slides up and down. The author finds it convenient to mold and burn his own liners.

leads. The whole cost is a mere trifle compared to the price one must pay for such a furnace made to order. The muffle is rectangular; it is $8\frac{1}{4}\times6\frac{1}{2}\times14$ inches. The furnace shell is 14 inches deep to fit the length of the muffle. It is $16\frac{1}{2}$ inches wide and 15 inches high. To hold such a furnace at any desired temperature from 200° C. to 1000° C. the current should be controlled with a dimmer or rheostat of from at least 12 to 2.5 amperes and a resistance of not less than 60 ohms.

CHAPTER XX *

PART V

SOME IMPROVED ELECTRICAL LABORATORY APPARATUS

I. Quick-heating Electric Furnace for the Determination of Carbon in Steel, etc., with Train.—The train (Photo No. 8, page 278) consists of (1) a mercury tube to detect leaks and stoppages: (2) a safety jar containing a 1 : 1 solution of KOH; (3) a tower filled loosely with a plug of glass wool followed with anhydrous calcium chloride, a layer of soda lime and another plug of the wool; (4) a jar of short pieces of stick caustic potash with a plug of glass wool at the top and at the bottom; (5) a clay and rubber connector doing away with rubber stoppers at the charging end; (6) the vitrified clay combustion tube with the tapered outlet doing away with the rubber stopper at this point also; (8) is the jar of granulated zinc to stop acid and sulphur; (9) is a jar of phosphoric acid powder and (10) is the bulb for absorbing and weighing the CO_2. This train was designed by the author, being a simplification of his train described in J. Am. Chem. Soc., May, 1908.

The author has now used the tapered clay combustion tubes for over six years for the determination of carbon in steel, etc., and has been using them for oxygen determinations also.

The new split muffle type of furnace was designed by the author. It is of most simple construction, consisting of a split muffle of kieselguhr, a coil of ni-chrome wire embedded in alundum cement as a replaceable heating element, and a supporting stand. The furnace will heat from the cold to 1000° C. in twenty to twenty-five minutes with a current consumption of 3 to 4 amperes. It can be cooled rapidly, if desired, by lifting off the top half of the split muffle. The author supplanted for some time in this laboratory, and in another laboratory under his direction, all of the type introduced by him in 1908* with this new type shown in Photo No. 2, page 89, and Photo No. 3, page 119.

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* Reprinted from the Journal of Industrial and Engineering Chemistry, Vol. VII, No. 11, page 960, November, 1915.

This type of electric furnace can be built in any length of heating surface with coils connected in parallel. The type shown in Photo No. 2, page 89, is 13 inches long by $3\frac{5}{32}$ inches outside diameter and $1\frac{15}{16}$ inside diameter. The author built the same type for organic work 18 inches long. By using three rheostats a long furnace can be made to heat to three different temperatures at once or it can be heated in one part if desired.

The furnace presents a bright neat appearance with its white muffle; new heating elements can be kept in stock and quickly put in place in case of a burn-out, as there are no screws or powdered heat insulation to bother with. In case the muffle becomes soiled it can be put in a muffle furnace and heated to a red heat for about twenty minutes, when it becomes as white as new. The simple construction makes the furnace a very inexpensive one.

By using a split insulation muffle of $5\frac{5}{8}$ inches outside diameter and $2\frac{5}{32}$ inside diameter, the author obtained a furnace of this type which is developing 1020° C. with a current consumption of only 2.7 amperes.

II. A New Type of Portable Laboratory Rheostat.—Photo No. 3, page 119, shows the rheostat designed by the author with a view to making repairs more easy and to have a piece of apparatus with sufficient capacity to fill the needs of most laboratories.

The rheostat occupies but a few inches of table width and can be set behind the other apparatus as illustrated in Photo No. 7, page 276. Repairs are easily made and the white frame of hard asbestos board gives a cheerful effect. If desired, two such rheostats can be bolted together, making a double instrument. The rheostat is practically indestructible so long as its capacity is not exceeded as there is nothing about its design to get out of repair.

* J. Am. Chem. Soc., XXX (1908), 773.

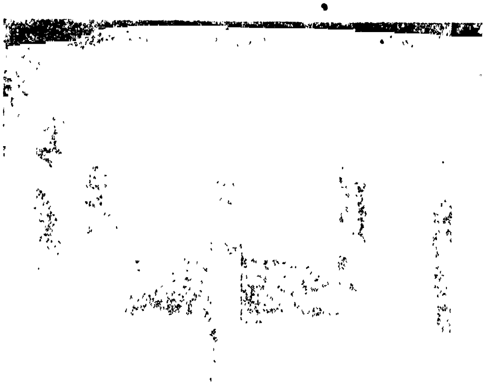

Photo 54.

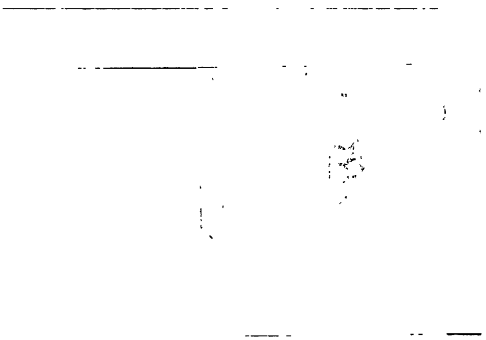

Photo 53.

CHAPTER XX

Part VI

RHEOSTATS AND LARGE FURNACE FOR HEAT TREATING

Photo No. 3, page 119, shows a rheostat suitable for a heat-treating or ignition laboratory muffle furnace with a muffle of

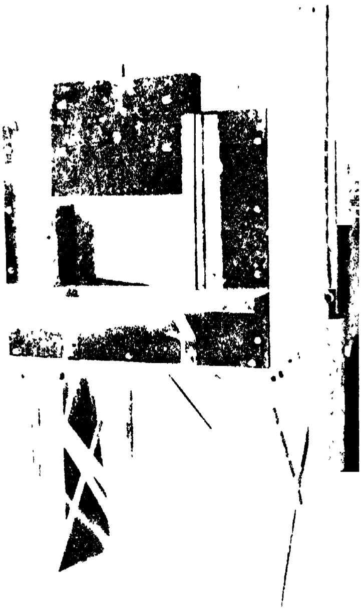

Photo 55.

14×5½×7½ inches, Photo No. 4, page 119. It will control a maximum current consumption of 15 amps. at 220 volts, giving

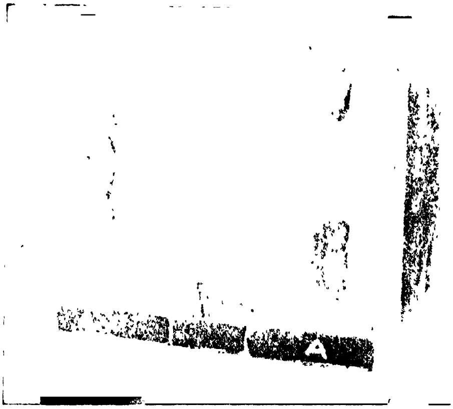

Photo 56.

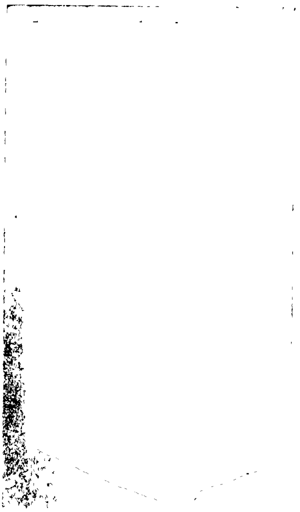

Photo 57.—Detail of muffle shown at M in Photo No. 56.

any temperature of 300° C. or less, to 1100° C., without the rheostat wires overheating. It consists of ten steps of $2\frac{2}{5}$ ohms (about ten coils of 9 feet each, ni-chrome wire of 15 gauge); nine coils $4\frac{1}{2}$ feet, each 15 gauge (about 10 ohms) and two coils of 6 feet, each 11 gauge (about 0.9 ohm), making a total of 30.9 ohms. Phœnix or Climax wire will answer just as well as ni-chrome except when exposed to dampness and fumes, in which case the ni-chrome does not rust away so soon. This rheostat must be connected in series with the furnace and the internal resistance of the furnace must be at least about 18 ohms at 220 volts.

PHOTO 58.

Photo No. 5 shows a rheostat suitable for an electric carbon combustion furnace such as is given on page 278. It has eleven steps consisting of one coil of 8 feet, 14 gauge, equal 1.27 ohms, and ten coils 5 feet each, 17 gauge, equal to 16 ohms or a total of 17.3 ohms. Internal furnace resistance should be about 29 ohms.

Photo No. 54 shows how two rheostats can be arranged on one supporting frame.

Photo No. 55 shows a large heat-treating muffle furnace with a muffle $7\frac{1}{2}\times 11\frac{1}{2}\times 26$ inches. Photo No. 56 shows how the brick are arranged. At *A* are infusorial brick; at *B*, *B*, *B*, are refractory fire brick. Photo No. 57 shows the rheostat to control this furnace, which consumes about 30 amperes at 220 volts. The rheostat contains 114 coils of 15 gauge Driver-Harris No. 194 nickel steel wire. These coils arranged, in steps consisting of three coils of 25 feet each (in parallel) per step, and each of thirty-eight such steps are connected in series with each other, and the entire rheostat is connected in series with the furnace. Photo No. 58 shows the arrangement of the top of the rheostat.

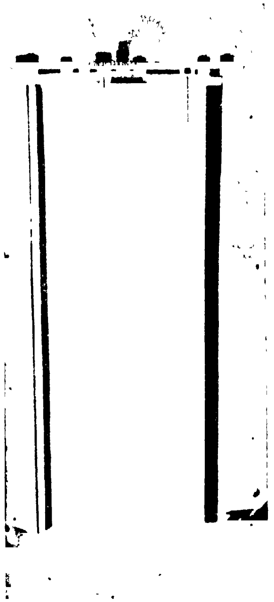

PHOTO 57.

CHAPTER XXI

PART I

AN AUTOMATIC STEAM WATER STILL

AFTER submitting to considerable annoyance from several types of water stills, the author decided to try steam coils as a source of heat.

The boiling of water by this means is not a new idea, but after more than a year's trial, there was finally evolved a form of still which has proven so satisfactory and the flow of the water has been so abundant that the details of the apparatus may be of assistance to someone else. (1908.) This type still in use (1920).

Two of these stills are in use in our laboratory, operating but part of each day. The supply is ample for all analytical needs and for drinking water, which is also furnished to a large office force.

Cold water from the tap enters the condenser jacket *C*, Fig. 59, through the cock *A*. The condenser jacket is a cylindrical copper vessel 11 inches in diameter and 15 inches high. The cooling water overflows at *B* to a sink not shown. A glass * tube siphon S', S'', S''', dipping into the water slightly below the level of *B*, carries hot water continually to the heating chamber *D* by way of the large copper feed funnel F', F''.

When the water in *D* has risen several inches the steam is turned into the worm coils of *D* at the valve *V*. These coils consist of two 12-foot lengths of three-quarter inch bore copper pipe,† brazed together and coiled around the inside walls of *D*. The steam from the boiling water rises into the dome and passes off through a block tin condensing pipe of five-eighths inch * inside diameter at *T* and travels through this pipe, which is coiled in a worm as shown in *C*.

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* A brass tube is now used, as it is more durable.

† The outside diameter of the copper pipe is $1\frac{1}{16}$ inches and the wall is $\frac{1}{8}$ inch.

The tin pipe passes through the tubular outlet *O'*, *O''* and delivers the distilled water on an absorbent cotton filter supported by a 6-inch ribbed glass funnel *W*. The filter catches any oily matter or other particles carried over with the steam.

The distillate is delivered to the receiving funnel at the rate of one liter every three minutes when sufficient pressure is maintained in *D* to keep the copper funnel *F'*, *F''* filled nearly to overflowing with hot water.

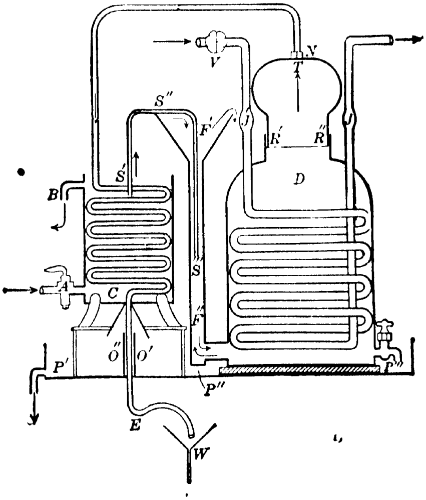

FIG. 59.

The water reservoir is a 9-gallon bottle, in the neck of which the funnel *W* rests. The bottle, which is not shown, is inclosed in a cupboard in which is an electric light to dispel darkness and roaches. This bottle rests in a copper pan, which is drained to the sewer. The tin pipe is bent into an elbow at *E* so that any condensation of moisture on damp days drips off at *E* instead of running down the pipe into *W*.

---

* The larger the inside diameter of the tin worm the better to secure rapid condensation and a large output of water.

The block tin worm now in use is $\frac{15}{16}$ to 1 inch outside diameter; $\frac{1}{8}$ to $\frac{5}{32}$ wall; and $\frac{3}{4}$-inch bore. The regular commercial sizes approximating these dimensions are used. A number of these stills are now in use. The worm is 28 feet long.

Steam pressure furnished from the mills is liable to continual variation. The amount of pressure may be nicely adjusted at *V*, but subsequent increase of pressure often causes the water to boil ever at *F* and splash down into the copper pan P', P'', P''', which is drained at P'. The pan is 5 inches deep and large enough to contain the entire apparatus.

To clean the still the tin pipe is unscrewed at *N*, the dome head is removed, and water is played on the interior of *D* with a hose, washing the sediment out through the cock at P'''.

The steam dome rests in the neck of *D* and is calked steam tight with cheese-cloth. The cloth is stretched in a diaphragm across R', R'', with enough excess of cloth for calking purposes.

The boiling of the water in F', F'' in no way prevents the action of the siphon S', S'', S'''. The heating coils of *D* are joined to ordinary steam pipes of the same diameter at J', J''.

This still could be made in any size to suit a greater or less production than that mentioned, a smaller size for a household or small laboratory, and in larger sizes for office buildings or for manufacturers needing a large supply of distilled water. A number of these stills are now in use.

CHAPTER XXI

PART II

CLAY COMBUSTION BOATS

THE clay boats are made from Klingenberg clay.* A typical analysis of it is given herewith:

	Per cent
Protoxide of iron	2.67
Silica	52.48
Alumina	29.46
Ignition loss	14.18

Any plastic clay of similar analysis free from grit would answer just as well. The clay is ground to pass a 30-mesh sieve, and is thoroughly kneaded to a stiff dough with water. It is then rolled in a towel. By wetting the towel occasionally, the clay can be kept ready to use as long as desired.

The clay is rolled on a moist plaster-of-paris slab into a cigar shape and pressed into the plaster-of-paris mold with the thumbs. The excess clay is scraped off with a thin-edged piece of wood. The guide strip is then laid on the mold. It is the exact duplicate of the face of the mold, or *pmno* as shown in the plan. This strip, of course, has an opening in it coinciding exactly with *IcdJ*, Fig. 60. The strip can be fastened on by a gum band at each end. The wooden tool *T* is plunged down through this slot, and, while being held perfectly vertical it is slid along the wooden guide strip, scooping out the clay and shaping the interior of the boat. The tool slides along the strip on its surfaces at *R* and *R'*. The distances from *c'* to *R* and from *R'* to *d'* are equal and conform to the thickness of the guide strip. The distance *c'd'* equals *cd*. *c'V* and *V'd'* regulate the thickness of the walls of the boat. *Vf'V'* forms the interior of the boat. The tool *T* is rounded on one side and is trimmed to a thin edge on the rounded side. The tools are kept in water, when not in the operator's hand, to prevent the clay from sticking to them. The interior of the mold has a flat bottom: The author prefers a boat of the following outside dimensions when burned: 15 mm. wide at top by 7 mm. wide at bottom by 9 mm. high by 131½ mm. long

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* A blend of clays gives better results.

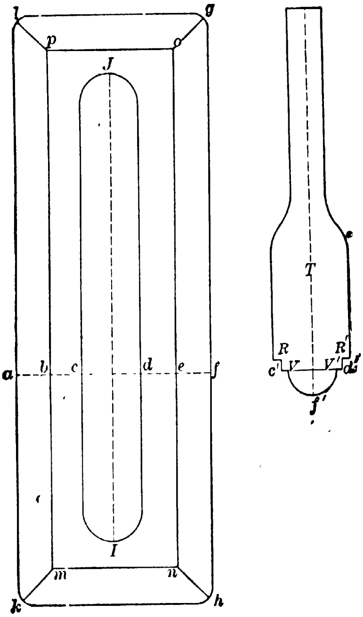

Fig. 60.

The bowl of the mold should be about 6 per cent larger in all its dimensions to allow for shrinkage.

After the interior has been properly shaped, the guide strip is removed, the face of the mold scraped clean, and the mold put away in a warm place for the clay to dry. Slow drying for one or two days is the best. When the boats no longer seem damp to the touch, they are removed from the molds and dried for several hours in an air bath at a temperature of 120° C. They are then put in a muffle furnace, and the latter is lighted and the heat brought slowly to a temperature of 850° to 900° C. (very bright red-heat) and kept at that temperature for from two to four hours. The heat is then turned off and the boats are ready for use. A boy can easily mold forty boats in three hours, and, after the molding is completed, the remaining operations require but a few moments' attention to make the transfers from the drying space to the air bath, and from the latter to the muffle furnace.

The boat should have walls and bottoms about one-sixteenth inch thick. Boats made as described answer all of the purposes of porcelain boats, and, one can readily see, are extremely cheap.

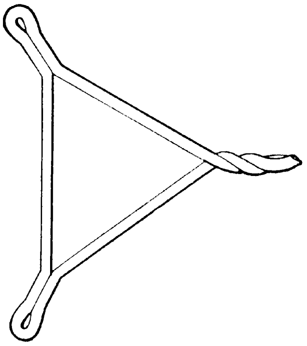

Fig. 61.

The author first experimented with a view to making his own boats, more than twelve years ago, and has used them for all combustion work ever since.

It is convenient to have the dimension *Kh*, 62 mm.; *hg*, 177 mm., and the total thickness of the mold 25 mm.

When the boats have been burned, two or three from each batch should be placed in the combustion furnace and a blank analysis made. If the weighing apparatus shows a gain of more than 0.0002 gram, it is an indication of imperfect burning of the boats. They should be reburned until free from all carbonaceous matter.

The Ni-chrome One-piece Triangle.—Fig. 61 shows a one-piece triangle designed by the author which anyone can make in a few minutes from the well-annealed ni-chrome wire. It is practically indestructible. The one shown was made from No. 8 gauge wire.

Sanitary Laboratory Wash Bottle.—Fig. 62 shows a wash bottle that is much used in this laboratory for washing precipitates. It has the advantage that the lips do not touch it. It is operated by a slight push of the thumb on the rubber bulb *A*. The little tube at *P* enables the operator to relieve pressure instantly when a washing is finished, avoiding spattering of the washing fluid and excessive amounts of the wash per application.

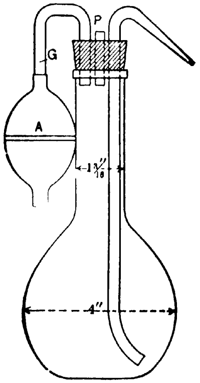

Fig. 62.

The rubber bulb is attached to the glass tube *G*. The capacity of the flask is 500 c.c. It has a fire-finished ring neck and takes a No. 6 rubber stopper.

CHAPTER XXI

Part III

LABORATORY REFRACTORIES

Laboratory refractories should be of such design and composition that they will stand rough usage and sudden expansion and contraction. This is especially true of boats for carbon combustion determinations; muffles for ignitions; Bunsen burners of the Chaddock type, chimneys for Argand burners, combustion tubes, pyrometer protection tubes, and crucibles.

Combustion Boats.—The combustion boats should also be of such composition that iron oxide and lead oxide do not slag with the walls of the boats at temperatures approaching 1100° C., to an appreciable extent. A well-designed boat of the proper composition, burned at the correct heat in the kiln, of the correct size and filled about half full of some neutral body like crude oxide of zirconia, or chrome iron ore, or some other suitable well-ignited metallic oxide of high fusing point—a boat of this type and so protected will be good for from 500 to 600 carbon combustions of steel. It should be said also in this connection that there is nothing gained by running the oxygen at a high rate of speed or by running the combustion furnace at temperatures in excess of 1000° C. Some chemists have a mistaken idea that the temperature must be such as to entirely melt up the sample of steel. This procedure not only will destroy any combustion boat in a few runs, but often cause low results due to unburnt steel occluded by the suddenly formed slag and perhaps due to the formation of some CO.

Photo No. 63 shows six sizes of boats which offer ample range in capacity for any laboratory's needs. No. 1 is $\frac{10}{16} \times 4$ inches; 2, $\frac{11}{16} \times 4$; 3, $\frac{12}{16} \times 4$; 4, $\frac{10}{16} \times 5\frac{1}{4}$; 5, $\frac{11}{16} \times 5\frac{1}{4}$; 6, $\frac{12}{16} \times 5\frac{1}{2}$.

Combustion Tubes.—Photo No. 64 shows three sizes of combustion tubes of the author's design which he has used in several laboratories under his direction for a number of years. The composition should be such as to be non-porous under pressure; not readily attacked by metallic slags, and vitrifying in such a way as to withstand rupture when cold bodies are repeatedly charged into it when it is at a high temperature. It is also a great advantage to have it of such composition as to not conduct away heat at the projecting ends like fused silica tubes, thereby avoiding a large loss of the expensive electrically supplied heat; also avoiding the nuisance of cooling devices at the ends that project from the furnace.

The convenient sizes are 24×$\frac{3}{4}$ inches inside diameter by 1-inch outside diameter with tapered ends; also 27 inches long by $\frac{15}{16}$ inside diameter by 1$\frac{1}{4}$ inches outside diameter, also a middle size $\frac{14}{16}$-inch bore×27 inches long. The author has found that the larger bore tube with the thicker wall lasts longer; although either size should last for months if the foregoing conditions are fulfilled. A good heavy wall tube of proper composition should last six months or more even though in daily use with a daily run of from 80 to 180 combustions.

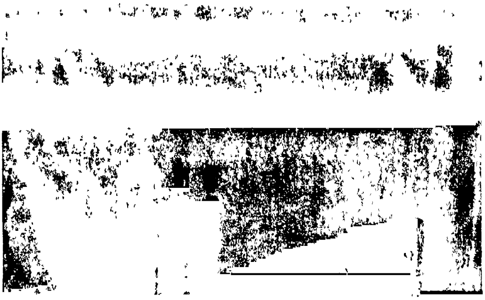

Photo 63.

Chimneys for Argand Burners.—Photo No. 63 also shows convenient chimneys for Argand burners. Here, again it is especially necessary to have a composition that will not crack with sudden changes of temperature. A chimney of proper

PHOTO 64

composition is non-crackable and will last for years as far as heat cracks are concerned. Two convenient sizes are No. 8 and No. 9; in photo No. 63, No. 8 is designed to be used in the sulphur apparatus given on pages 331-332.

Porous Filtering Crucibles.—At No. 7 in photo No. 63 is shown a porous crucible. Such a crucible should be of sufficiently open grain to permit the passage through its pores of turbid fluid to its total capacity in fifteen seconds, when mild suction is applied, i.e., ordinary one-quarter inch bore one-sixteenth inch wall tubing should not collapse; and the filtrate should be perfectly clear and sparkling.

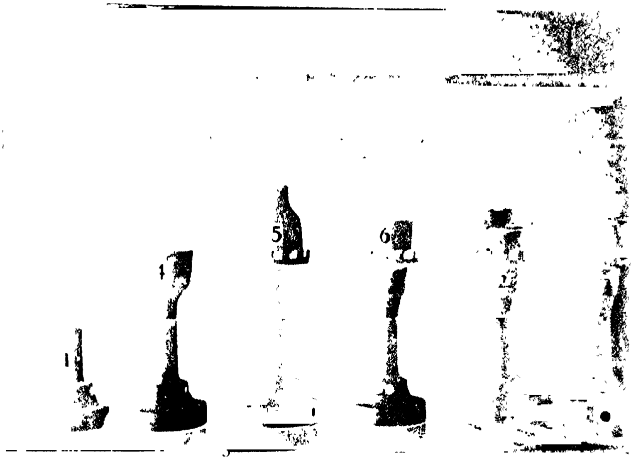

Photo 65.

New Modified Refractory Bunsen Burner of the Chaddock Type.—The author has designed the modified Chaddock with the following new features. 1 in Photo No. 65 shows the burner proper; 4 shows the bell-top chimney, which can also be used as a crucible cover to raise the temperature around the whole crucible at 5. This bell top can also be inverted and used as an extension support as shown at 6. At 2 the rubber hose is shown entering at a half-round opening. This makes the setting of the glass nipple tube much easier, as anyone will appreciate who has used a Chaddock.

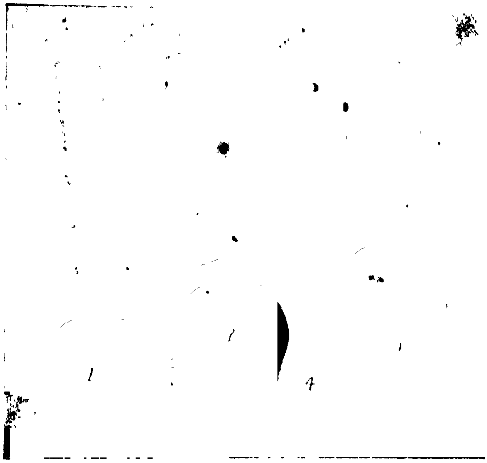

Photo 66.

Photo 67.

This style of burner should be made of a mixture of refractories that will not crack with suddenly applied heat. A proper selection of materials will secure immunity from heat cracks.

Kipp Apparatus Consisting of Three Replaceable Parts.—The author designed an apparatus for generating H, H_2S, and CO_2 of the Kipp type, consisting of three replaceable parts, and of acid-proof stoneware. The bottom part holds 2500 c.c. and the top bulb 2000 c.c. The total height is 23 inches. The parts are interlocking and connected together with acid-proof cement (see Photo No. 66); making the whole apparatus perfectly rigid as though of one piece. The advantage of the apparatus lies in its replaceable parts. If one part be broken a new one can be put in its place making the generator is like new. The parts are very strong, being of heavy stoneware. The separate parts are shown in Photo No. 66 and the complete generator in Photo No. 67.

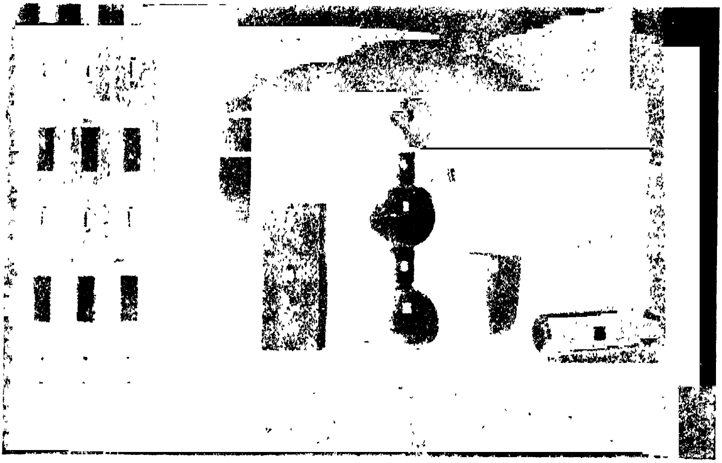

Photo 68.

Photo No. 69 shows how this Kipp can be made in four replaceable parts. The inner tube passing through a rubber stopper to melt the top bulb 1 at 2 being joined to it by the rubber connector and also a copper clamp not shown, but which is screwed fast around the rubber sleeve at 2. Photo No. 70 shows a battery of these generators.

Muffle, Assay Crucible, and Heat Insulation, Split Cylinder of Infusorial Earth.—The above are shown in Photo No. 68 at 6, 7, and 8, respectively. The dimensions of the muffle are 14×5½ ×7½ inches. The crucible is 6 inches top diameter by 9 inches high by 4 inches bottom diameter. The split cylinder is 1⅞ inches inner diameter by inner diameter by 12½ inches long. The latter is the heat insulation jacket for the carbon combustion furnace shown on page 278.

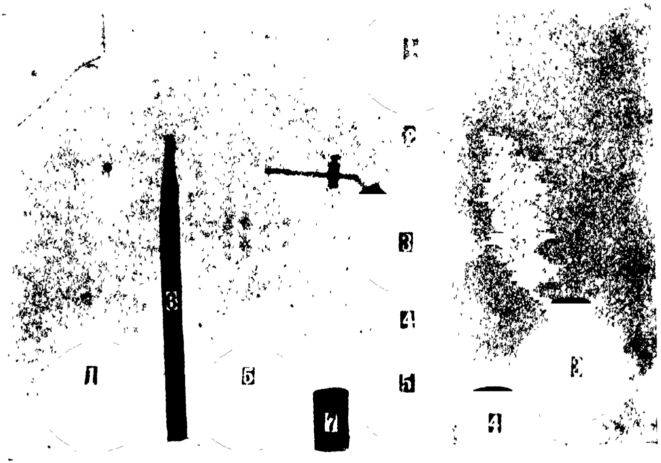

PHOTO 69

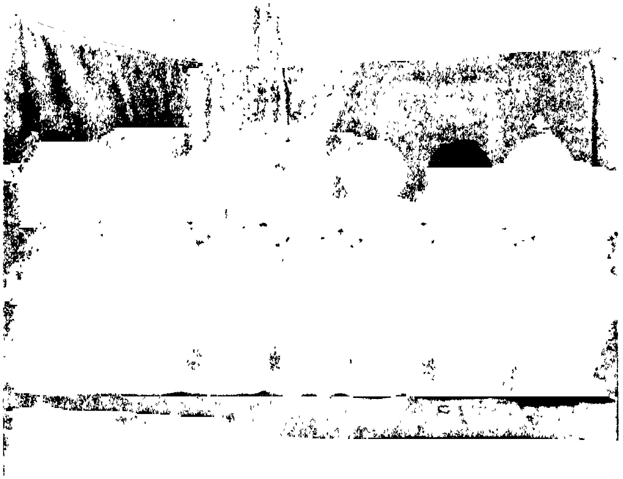

PHOTO 70.

CHAPTER XXII

PART I

ENGLISH CHROME-VANADIUM STANDARD STEEL "V."

THIS standard was analyzed by twenty-five English and three American laboratories. The reports were handed in blind. Nothing more was heard of the matter until the printed report was mailed to the co-operating chemists together with a very generous portion of this valuable standard (October, 1919).

It is interesting to note just how closely the three American chemists came to the general average of all of the results:

LABORATORY:	% C	% Si	% S	% P	% Mn	% Cr	% V
U. S. Bureau of Standards	0.559	0.152- 0.170	0.059	0.028	0.534	0.859	0.278
Baldwin Locomotive Works	0.563	0.174	0.060 0.059	0.021	0.532	0.890	0.270
CRUCIBLE STEEL CO. OF AMERICA:							
(*Park Works Lab.*)	0.554	0.170	0.064 0.065	0.024	0.540	0.860	0.275
General Average of All Laboratories..	0.548	0.161	0.063	0.024	0.542	0.861	0.273

Of course, Park Works results were obtained by the methods as given in the foregoing pages. See copy of Ridsdale & Co.'s report, page 530.

SECOND EDITION, containing additional tests of British co-operators and also those obtained through the courtesy of the Bureau of Standards Washington (per Dr W F Hillebrand, acting director) also a steel maker and a user in the U S A, each selected by the Bureau

British
Chemical Standards*

Certificate of Analyses
OF
CHROME-VANADIUM STEEL "V."†

Issued by Messrs. Ridsdale & Co. from the Laboratory and Technical Bureau, Wilson Street, Middlesbrough, Eng., under the auspices of the body of co-operating Analysts.

CO-OPERATING ANALYSTS OR FIRMS

REFEREE ANALYSTS – INDEPENDENT

No	Name	Place
1	**Herdman** W H Wellington Street	Glasgow
2	**Pattinson** J & H S (Per J T Dunn, *D Sc F I C*) Dean Street	Newcastle on Tyne
3	**Pattinson & Stead**, Queen's Square	Middlesbrough
4	**Ridsdale** & Co (Per C H Ridsdale, *F I C F C S* and N D Ridsdale, *F C S*) Wilson Street	Middlesbrough
5	**Riley (Edward) & Harbord** (Per C O Bannister *F I C A R S M*), Victoria Street	London

RAILWAY CHEMISTS – Representing USERS issuing SPECIFICATIONS

No	Name	Place
6	**Smith**, H Lancashire & Yorkshire Railway	Horwich
7	**Rowley**, E W, North Eastern Railway	Darlington

GOVERNMENT DEPARTMENTS.

No	Name	Place
8	**Admiralty Laboratories** (Per J C W Humfrey, *B A M Sc* M Eng, Chief Analyst)	Sheffield and other centres
9	**Minister of Munitions Laboratory**, Townhead Street	Sheffield
10	**Research Department, Royal Arsenal**	Woolwich
11	**United States Bureau of Standards** (Per (*a*) L F Witmer and (*b*) J I Hoffman)	Washington U S A

WORKS CHEMISTS—Representing MAKERS.

No	Name	Place
12	**Daw**, F W, *F I C A R C Sc*, Ebbw Vale Steel, Iron & Coal Co, Ld	Ebbw Vale
13	**Derby**, B Cammell, Laird & Co, Ld	Sheffield
14	**Duffy** I *B Met*, Sir J Jonas, Colver & Co, Ld	Sheffield
15	**Elliot**, T G, *F I C* Hadfields, Ld	Sheffield
16	**Graham**, C S, *F C S* J Lysaght & Co, Ld	Scunthorpe
17	**Hanson Weldon**, *F C S*, Clarence Steel Works	Middlesbrough
18	**Henshaw** P B, Kayser, Ellison & Co, Ld	Sheffield
19	**Howson, Richard**, Samuel Fox & Co, Ld	Stocksbridge
20	**Sillars** D, Bolckow Vaughan & Co, Ld	South Bank
21	**Thompson**, J L, Monk Bridge Iron & Steel Co, Ld	Leeds
22	**Wilkinson**, C North Eastern Steel Co Ld	Middlesbrough
23	**Wragg**, J H, *A I M M*, Samuel Osborne & Co, Ld	Sheffield
24	**Young**, H J, *F I C*, North Eastern Marine Engineering Co, Ld	Wallsend on Tyne
25	**Johnson**, C M, Crucible Steel Company of America	Pittsburg, Pa, U S A

MOTOR, AERO or LOCO MAKERS—Representing USERS

No	Name	Place
26	**Clermont**, J D, Napier & Son, Ld	London
27	**Hall**, H C *A I C M Met* Rolls Royce, Ld	Derby
28	**Baldwin Locomotive Co** (Per J A Hance, Engineer of Tests)	Philadelphia, Pa U S A

A & S —7369

ANALYST	CARBON PER CENT		SILICON PER CENT	SULPHUR PER CENT		PHOSPHORUS PER CENT			MANGANESE PER CENT			CHROMIUM PER CENT	VANADIUM PER CENT			ARSENIC PER CENT	ALUMINIUM PER CENT	COPPER PER CENT	Co, Ni, Mo, W PER CENT
	DIRECT COMBUSTION IN OXYGEN	POTASSIUM COPPER CHLORIDE SOLUTION AND COMBUSTION	SOLUTION IN *HCl* OR AQUA REGIA SINGLE EVAPORATION	TOTAL BY OXIDATION	EVOLUTION OF SULPHIDE WITH *HCl* AND TITRATION WITH IODINE	SEPARATION OF ARSENIC AS *As₂S₃* OR *AsCl₃* AND GRAVIMETRIC MOLYBDATE	ANALOID (1914) DIRECT MOLYBDATE ALKALIMETRIC FINISH (a)	DIRECT MOLYBDATE WITHOUT EVAPORATION ALKALIMETRIC FINISH (a)	BISMUTHATE VOLUMETRIC	ANALOID (PERSULPHATE VOLUMETRIC) AND OTHERS	IRON ACETATE SEPARATION AND GRAVIMETRIC *Mn₃O₄*	OXIDATION WITH *KMnO₄* VOLUMETRIC (*FeSO₄* & *KMnO₄*) FINISH	AFTER *Cr* EST COLD OXIDATION WITH *KMnO₄* VOLUMETRIC (*FeSO₄*) FINISH	HYDROGEN PEROXIDE COLORIMETRIC	ETHER SEPN FROM *Fe* & *NaOH* SEPN FROM *Cr* VOLUMET *KMnO₄*				
No 2		0·558	0·153 (b)	0·066		0·024		.	0·510			0·837			0·29 (s)				
„ 4	0·532 (d)(g)		0·172 (h) 0·167 (i)	0·061	0·064	0·023 (a)(p)	0·023 0·023 (n)	.	0·556	0·551		0·863		0·29	0·28 (t)				Ni nil
„ 5	0·550			0·066		0·022			0·536		0·525	0·840			0·31				
„ 8§	0·555	0·570	0·150 (h)	0·067	0·061 (k)			0·022 (m)	0·57			0·84	0·245	–	0·275				
„ 9§	0·550	0·560	0·155 (h)	0·062	0·060			0·023	0·56	Ford & Williams 0·55	0·57	0·86	0·29	0·28		no appreciable traces			
„ 10§	0·546 (d)		0·170	0·063				0·027 (a)(w)(b)	0·552	0·553	0·560 (c)	0·86	0·24	0·28	0·28 (c)	0·016		trace under 0·01	nil
„ 11 (w)	0·559		0·152 (i) 0·170 (b)	0·059				0·028	0·534 (x)			0·860 (y) 0·858 (z)	0·278 (u)						Ni 0·027
„ 12	0·54		0·16 (b)	0·063				0·025	0·54		0·54	0·86	0·28		0·27				
„ 15	0·55 (d)		0·16 (b)	0·068	0·067 (l)	—		0·027 (m)	0·52	Persulph Volumet 0·50		0·85	0·285 (v)			each under 0·02			W nil
„ 18	0·525	0·53	0·147 (b) 0·150	0·062				0·021 (b)	0·515	–	0·52 (r)	0·876	0·256	0·244		0·015	0·014	0·05	W & Ni nil
„ 23	0·57 (d)		0·140		0·061			0·021 (b)(m)	0·56			0·87			0·28				
„ 25	0·564		0·170 (i)(b)	0·065	0·064			0·024 (e)		PbO₂ Oxidation 0·54		0·86	0·275						
„ 26	0·535		0·173 (i)	0·061	0·060			0·020 (i)	0·545			0·870 0·866 (o)	0·266 (v)			0·016	trace	nil	Co & Ni nil
„ 27	0·53 (d)		0·175 (h)	0·060				0·025	0·57			0·885	0·268	0·270					
„ 28	0·563 (d)		0·174 (i)	0·060	0·059			0·021	0·532 (f)	Persulph Volumet Na AsO₃ 0·520		0·89	0·27						
Average	0·547	0·554		0·063	0·062	0·023	0·023	0·024	0·543	0·536	0·543		0·268	0·273	0·281	0·016			
General Average	0·548		0·161	0·063		0·024			0·542			0·861	0·273						

The results shewn for each Chemist are those which he has finally decided, after careful consideration of his repeated checks, are correct.

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* For brief description of the movement see articles in *Iron and Coal Trades Review* of September 28 1917 and March 8 1918 also paper given before Soc Chem Industry Birmingham November 27 1918 (*J S C I* February 15th, 1919) Notes on Chemical Standards and their bearing on the Unification of Analysis.

† **The Standard Bar was kindly provided by Messrs Kayser Ellison & Co Ld Carlisle Works Sheffield being specially selected on account of its homogeneity**

§ **The Admiralty** War Office and Ministry of Munitions wish it to be made clear that the homogeneity of the bulk of standardised turnings represented is not in any way guaranteed by them

(a) Titration with standard *NaOH* and HNO_3
(b) Weighed as $PbMoO_4$
(c) Arnold & Ibbotson's combined method
(d) Mixed with either red lead crushed firebrick or alumina
(e) See Journal Ind & E Chem February 1919
(f) Cain's Method U S Bureau of Standards
(g) Residue crushed and re burnt
(h) Ppt treated with *HF*
(i) Yellow ppt converted to $Mg_2P_2O_7$ i e 0·071%
(j) Brown's method or other modification evaporating to SO_3 fumes
(k) 0·006% S found in residue after evolution
(l) Annealed at 750°C with $K_3Fe(CN)_6$
(m) Vanadium reduced with $FeSO_4$ and pptn at low temp

(n) Separation and fusion as in (y) then reduction *Zn* and $KMnO_4$ titration Allow for Cr
(o) Gregory method J C S Nov 1907
(p) As removed with *HBr* Proc Clev Inst Eng No 4 1918 19 & C News Feb 28th, 1919
(r) Finished off by bismuthate
(s) U S Bureau Circ No 14, 5th ed 1916 Method I p 16
(t) Phospho Molyb pptn H_2O_2 reduction Volumet $KMnO_4$
(u) Average of 2 rather different methods
(v) Electrometric titration
(w) Mean of the two Analysts results
(x) Cr & V first removed with $NaHCO_3$ from sulphate solution.
(y) Separation as in (x) fusion with Na_2O_2 and titration of CrO_3 as usual
(z) Persulphate oxidation and titration of CrO_3 as usual

RIDSDALE & CO.
(C. H. Ridsdale, F.I.C. F.C.S. & N. D. Ridsdale, F.C.S.)
1st October, 1919

CHAPTER XXII

PART II

SHORT METHOD FOR MOLYBDENUM IN STEEL

(Absence of Tungsten)

(*A*) Dissolve 3 grams of steel drillings in 50 c.c. 1:1 HCl. Warm until action ceases, then add a few crystals of potassium or sodium chlorate, that is, enough to dissolve all black residue on further heating.

(*B*) Boil down quickly to about 15 c.c. to remove excess of free acid, as molybdenum is not precipitated completely by H_2S in the presence of much free acid.

(*C*) Dilute to 150 c.c. with water.

(*D*) Pass a rapid stream of H_2S for about fifteen minutes. Filter off sulphide. Wash the same thoroughly with H_2S water.

(*E*) Burn off the sulphide in a porcelain crucible at a heat *not exceeding* 550° *C.* until all char is gone. Cool, and weigh. This weight represents the molybdic oxide, plus a little silicon plus copper oxide, tin oxide, etc.

Extract this ash with 40 c.c. of filtered ammonia. Warm in the crucible until the residue is light and floats easily, showing that all of the heavy molybdic oxide has been dissolved. Filter again.

Wash with ammonia water thoroughly so as to remove all molybdenum. Ignite at a red heat and weigh again. The difference between this weight and the first weight equals the weight of the molybdic oxide present, plus any copper dissolved by the ammonia. Tin oxide is not dissolved.

If the filtrate from the ammonia is blue, copper is present and for very accurate work, a correction must be made. This correction is usually small, and unless the filtrate is very deep blue, can be dispensed with, especially when bath tests are being run.

If the correction is to be made, the filtrate is made slightly acid with hydrochloric and evaporated to a low volume and made *faintly* but distinctly alkaline with ammonia.

The copper determination is then finished by titrating to the disappearance of the blue color with standard KCN solution in the same manner as for copper in steel. The copper thus found, is calculated to CuO and deducted from the weight of MoO_3 plus CuO already obtained.

The remainder is figured to Mo by the factor 0.6666.

Omitting the copper correction, this method can be carried through, in duplicate, in 2 hours.

This method assumes the absence of tungsten. If tungsten be present in sufficient quantity to separate out as yellow residue, then after (*C*), it should be filtered out, washed, and the filtrate and washings finished as given in (*D*) and (*E*). The WO_3 can be examined for MoO_3 if much W and Mo be present in the steel.

CHAPTER XXIII

PART I

The Analysis of Ferro-cerium and Cerium Steel.—The determination of large quantities of cerium (the mixed metals of the cerium group) is comparatively simple, but to determine, gravimetrically, a small amount of cerium in the presence of a large amount of iron is fraught with many interferences. Any attempts in this laboratory, for example, to precipitate ten to twenty milligrams of cerium content away from 5 grams of iron have thus far resulted in the precipitation of a large portion of the iron with the cerium, or a large amount of iron and no cerium with it. This is true whether the attempt be made either by the phosphate method or the oxalate method. The iron interferes at all points, when it is present in large excess. The volumetric methods to be described later are the only quantitative methods for small amounts of cerium thus far developed in this laboratory when large amounts of iron are present. Both methods are interfered with by the presence of chromium, and one is interfered with by the presence of both chromium and manganese.

Cerium in Ferro-cerium (Gravimetric)

The author uses the well-known method of precipitating the cerium (mixed cerium group) away from the iron (less than a gram of iron present) in nearly neutral sulphate solution with a saturated solution of ammonium oxalate.

Dissolve one gram of the ferro-cerium in 50 c.c. of 1.20 sp. gr. nitric acid; evaporate to dryness; ignite to destroy the nitrates; dissolve in conc. HCl; dilute and filter out silica. Wash the insoluble silica; ignite it to an ash; weigh it; remove the silica with HF and a few drops of conc. H_2SO_4 as in silicon in steel. Fuse any residue left in the crucible from the HF evaporation with sodium carbonate; dissolve in HCl; fume it with H_2SO_4; add water; heat until the sulphate is dissolved and add the solution to the main filtrate and washings obtained from the first

This main filtrate will now contain all of the cerium. It is nearly neutralized with 1 : 1 ammonia water, and to the cold solution which should now be of about 400 c.c. volume, 50 c.c. of a saturated solution of ammonium oxalate are added and the cerium oxalate is allowed to settle for about two hours; it is filtered; washed with ammonium oxalate water; ignited to the reddish cerium oxide (CeO_2) which contains 81.42 per cent Ce. This reddish oxide may contain some iron so it must be transferred to a porcelain dish; gotten into solution with HCl (chlorine forms hence the removal from the platinum crucible before dissolving); converted to sulphate and passed through the zinc reductor. The iron so found is deducted from the CeO_2 before calculating to Ce.

MANGANESE

Manganese interferes with the gravimetric determination of cerium and cerium interferes with the volumetric and gravimetric determination of manganese. Cerium and chromium oxidize to a higher oxide with PbO_2. If zinc oxide is used the cerium, unlike chromium, is largely in the filtrate with the Mn. On peroxidizing it remains on the filter with the manganese and iron. If the author's scheme of fractional precipitation with ammonia in reduced solution be tried, the cerium will still be found with the iron and manganese. (This, however, is a separation from chromium as the chromium is precipitated. See page 30.) Vanadium can also be separated from cerium by the ammonia fractional precipitation. The following recoveries were gotten when the amounts of cerium, vanadium and chromium were added in 5 grams of steel and the steel was then dissolved in 50 c.c. of 1 : 3 H_2SO_4 and 50 c.c. of water. The ammonia separation was made as described on page 30, the ammonia being added until the greenish gray chromium hydroxide settled down well:

Cerium present gram	Cr Added gram	Cr Found gram	V Added gram	V Found gram
None	0 1057	0.01057	0.0765	0.0765
0.020	0.1057	0.1066	0.0765	0.0767
0.060	0.1057	0.1072	0.0765	0.0762
0.080	0.1057	0.1079	0.0765	0.0784
0.320	0.1057	0.1084	0.0765	0.0769
0.505	0.1057	0.1087	0.0765	0.0754

Evidently from this table a little cerium was dragged out with the chromium but the vanadium results are very satisfactory. To secure an absolute separation of the cerium from the chromium, it is necessary to peroxidize the sulphuric acid solution of the chromium-vanadium precipitate obtained by the ammonia. This leaves the small amount of cerium with some iron on the filter and the chromium and vanadium in solution as sodium salts. The small amount of cerium and iron can be dissolved in sulphuric acid and be added to the main iron and cerium solution. This sulphuric solution can then be evaporated to 350 c.c. and finished volumetrically by the methods to be described. The vanadium and chromium can then be finished as described under ferro-vanadium and chromium-vanadium steels.

MANGANESE

Cerium does not begin to interfere seriously with the determination of manganese in cerium steel by the lead peroxide method until it is present in excess of about 1 per cent of Ce.

To remove the cerium proceed as follows:

Weigh 0.4 gram of the steel or ferro-cerium, if the manganese does not exceed 0.50 per cent Mn, or a correspondingly less amount for higher percents of Mn, and get it into solution with 20 c.c. of 1 : 3 H_2SO_4; and 20 c.c. water; oxidize with 20 c.c. of 1.20 nitric acid; make a basic acetate separation as given for manganese in ferro-manganese but avoid using any HCl.

To the filtrate and washings from the basic acetate separation of the iron, chromium, etc., add 5 grams of ammonium persulphate crystals and boil three or four minutes; then add an excess of ammonia and boil again until the dark-brown precipitate of the hydrated oxide of manganese separates out well; filter it off, mixed with a little paper pulp; wash thoroughly with persulphate water containing a little ammonia. Then treat the precipitate on the filter with 35 c.c. of ferrous ammonium sulphate solution mixed with an equal volume of 1 : 3 sulphuric acid; use this solution warm, if necessary.

The ferrous ammonium sulphate is made by dissolving 2 grams of the salt in 100 c.c. of water. Wash the pulp, which should now be nearly, or entirely, white, with water containing a little sulphuric acid. Wash about thirty times. The filtrate and washings should be concentrated, if necessary, to 100 c.c. Then add 50 c.c. of conc. nitric acid and bring to boil; add 2 grams of light-brown lead peroxide; and boil five minutes in the 400 c.c. beaker; filter through washed asbestos; wash out pink color with distilled water; cool and titrate to disappearance of pink color with the arsenite standard used in steel.

This method has been tested on standards containing chromium up to 1 per cent and cerium added up to 7 per cent Ce, and exact results for manganese were obtained. 1 c.c. of the arsenite equals about 0.07 per cent manganese when 0.100 gram of sample is used.

VOLUMETRIC METHOD FOR CERIUM IN STEEL AND FERRO-CERIUM: BY OXIDATION WITH LEAD PEROXIDE

(Absence of Chromium)

Dissolve 5 grams of steel or ½ gram of ferro-cerium in 70 c.c. of 1 : 3 H_2SO_4; oxidize by heating with 45 c.c. of 1.20 sp. gr. nitric acid. Add the nitric acid a little at a time. Heat until all red fumes are gone. Then add 2 to 3 grams of lead peroxide of the light brown variety. Boil in the 600 c.c. beaker for fifteen minutes.

Filter on a washed asbestos filter of the same type as used for rapid manganese tests. Filter cold. If the filtrate looks pink some manganese has been oxidized to the manganic or permanganic state and must be reduced by adding to the filtrate a little ammonium-persulphate. Add 50 milligrams and boil gently, adding a few grains of precipitated silica to prevent boiling over of the solution. Boil twenty minutes. Remove from the fire and add another 50 mgs. of ammonium persulphate, if necessary, and repeat the boiling and so on until the pink color suggesting the color of permanganate of potassium is gone. If during these operations the solution becomes slightly cloudy due to the formation of manganese oxide, the same must be filtered through washed, ignited asbestos again, washing with water containing some dilute nitric acid wash. The clear, cold filtrate is now ready for the titration. The ferri-cyanide indicator is added as in the determination of vanadium in steel, and a standard solution of ferrous-ammonium sulphate is added from a burette until the same blue end-point is obtained, as in vanadium. Unlike the vanadium titration, this blue end-point does not get continually darker, once it is reached, as in vanadium, but has a tendency to grow lighter, owing to the action of the nitric acid.

This standard is one-fifth that of the one used for the titration of chromium in steel. One c.c. of it by this method should be equivalent to about 0.002 gram Ce to 0.0029 gram Ce, depending on the amount of iron and manganese present in the solution being titrated.

0.4722 gram of so-called C. P. cerium oxide dissolved in 20 c.c. 1.20 sp. gr. HCl; fumed with 50 c.c. of 1 : 3 H_2SO_4; diluted with water and heated until all was dissolved; then boiled with lead peroxide and titrated with the ferrous-ammonium standard gave a value of 1 c.c. equal 0.00235 gram of Ce; 0.2542 gram of cerium oxalate sold as C. P. ignited to the red oxide and finished in the same way gave 1 c.c. of the standard equal 0.00226 gram of Ce.

0.500 gram of ferro-cerium was put through as described for cerium and gave a value of 1 c.c. equal 0.0020 gram of Ce. Also the same value was gotten from another portion of ignited cerium oxalate. When 5 grams of steel are present and a blank is deducted higher values per c.c. of standard solution were obtained running as high as 1 c.c. equal 0.0038 gram of Ce. Therefore this method which is the best volumetric thus far tried in this laboratory must be carried out with about the same amount of iron present in the standardizing mixture as is likely to be in the sample to be analyzed. CHROMIUM MUST BE ABSENT as it is oxidized by the lead peroxide in the same way as the cerium and consumes a definite amount of the ferrous-ammonium sulphate standard, being proportional to the chromium present.

SECOND VOLUMETRIC METHOD FOR CERIUM IN STEEL AND FERRO-CERIUM

Proceed exactly as in the first method up to the point where the solutions are to be oxidized but instead of using lead oxide, a permanganate solution (1 gram of $KMnO_4$ dissolved in a liter of water) is added a c.c. at a time avoiding at all times an excess. This permanganate is titrated into the boiling solution in this way until finally a *slight* precipitate of manganese oxide is obtained that does not disappear after fifteen minutes' boiling. At this point 100 milligrams of ammonium persulphate are added, after cooling off the solution somewhat. The solution is again boiled for fifteen minutes to destroy any manganic condition that always forms during the foregoing operations. The solutions are then cooled; filtered and titrated as in the first volumetric method. After deducting blanks (which will run as high as 11 c.c. before a blue end-point is gotten on 5 grams of non-cerium steel) the same ferrous ammonium standard as used in the peroxide method will have a cerium value of 1 c.c. equal to about 0.005 gram of Ce. Chromium and vanadium interfere as stated and must be removed or corrected for, as already described in the first volumetric method. Pages 534 and 535.

CHROMIUM-VANADIUM STEEL WITH MUCH CERIUM

(*Several Per Cent of Ce*)

Get 1 gram of the sample into solution in the manner described on page 535 under Manganese. This solution will now contain all of the cerium in shape to remove all of the chromium, vanadium and tungsten by peroxidation as described under chromium in ferro-chromium, etc. This will require several peroxidations but in the end, the cerium and the iron will be on the filter, and the interfering elements will be in the alkaline filtrates.

The cerium and iron can be then dissolved off with sulphuric acid and the cerium finished by the lead peroxide method.

CHAPTER XXXIII

PART II

FURTHER MODIFICATION OF THE FEVERT CO_2 WEIGHING APPARATUS

IN the *Iron Age*, vol. 102, No. 8, is shown Stetser and Norton's modification of the original Midvale Absorption and Weighing Apparatus for carbon dioxide as designed by Mr. H. L. Fevert, of the Midvale Co. This "bulb" is shown in Fig. C, page 541. The author tried this apparatus in the laboratory of the Park Works and in the hands of a good man the bottom was knocked out after a run of 60 carbon combustions by a rather slight fall. The bottom or foot proved to be of very thin blown glass not as thick as an egg shell.

Knowing the proneness of expert glassblowers to blow bulbs of paper thin walls, he submitted to a well-known house in Philadelphia a drawing of a further modification of this promising CO_2 "bulb." This drawing is shown in Fig. D, page 541. This shows a bottom or foot of heavy glass which eliminates the frail design shown in Fig. C. The originators' have produced an apparatus that is simplicity itself. The author's modification is somewhat larger than original modification shown at C.

The author leads the products of the carbon combustion into this latest modification at the small tube shown about the middle of A in photo No. 68, page 540. "A" alone is weighed. "B" is used merely for a bubble tube, and containing KOH solution, acts as a guard against CO_2, getting into "A" via its outlet at the top of "A." This bulb according to the original scheme is filled with asbestos, saturated with sodium hydrate, and in dry granular form.

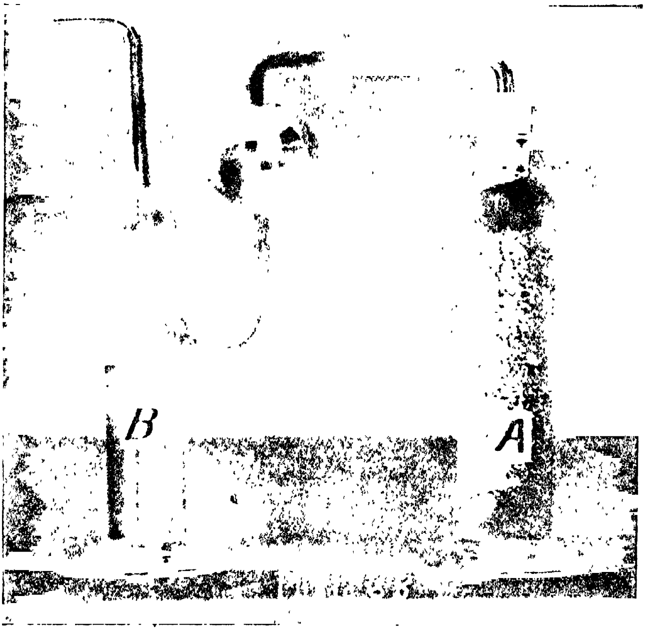

Photo No. 68

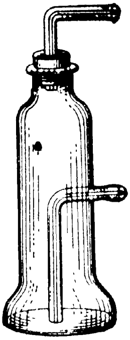

Fig C

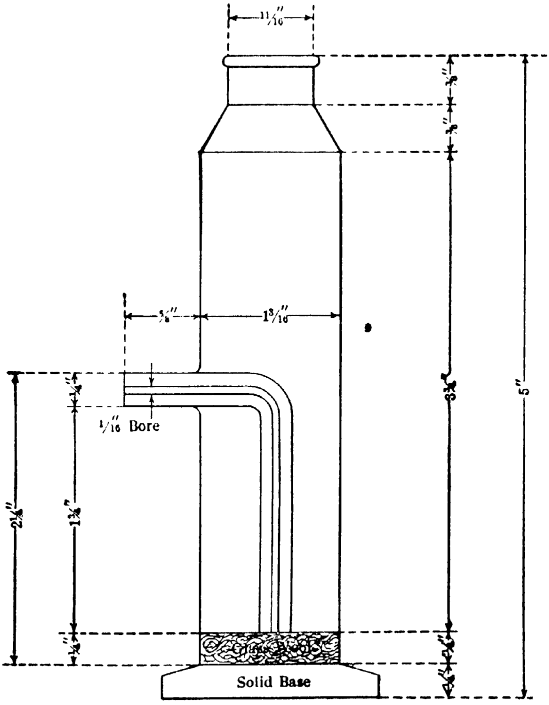
11/16"
3/8"
3/8"
5/8"
1 3/16"
1/4"
1/16 Bore
3¾"
5"
2¼"
1¾"
1/4"
1/4"
1/4"
Glass Wool
Solid Base

Fig. D

OF IN
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OF IN
1928

INTERNATIONAL ATOMIC WEIGHTS, 1920.

Elements.	Symbol	Atomic Weights.	Elements.	Symbol	Atomic Weights.
Aluminium	Al	27.1	Neodymium	Nd	144.3
Antimony	Sb	120.2	Neon	Ne	20.2
Argon	A	39.9	Nickel	Ni	58.68
Arsenic	As	74.96	Niton (radium emanation)	Nt	222.4
Barium	Ba	137.37			
Bismuth	Bi	208.0	Nitrogen	N	14.08
Boron	B	10.9	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.4	Palladium	Pd	106.7
Caesium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.005	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.9
Chlorine	Cl	35.46	Radium	Ra	226.0
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.1	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dyprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	70.1	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulphur	S	32.06
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.00	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.15
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	173.5
Lutecium	Lu	175.0			
Magnesium	Mg	24.32	Yttrium	Yt	89.33
Manganese	Mn	54.93	Zinc	Zn	65.37
Mercury	Hg	200.6	Zirconium	Zr	90.6
Molybdenum	Mo	96.0			

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